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(54) **Quinoline fungicides**

Fungicide Chinoline

Quinoléines fongicides

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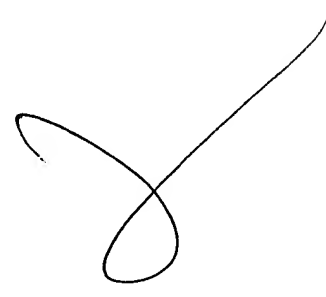
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EP-A- 0 029 319 GB-A- 1 233 938
GB-A- 2 135 887 US-A- 2 883 382

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abstract no. 87501u, Columbus, Ohio, US; &
JP-A-78 103 484 (TAKEDA CHEMICAL IND., LTD)
21-02-1977

Remarks:

The file contains technical information submitted
after the application was filed and not included in this
specification



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Description

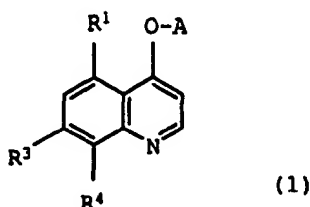
Background of the Invention

Field of the Invention

[0001] This invention provides new compounds that have excellent plant fungicide activity. Some of the compounds have also demonstrated insecticidal and miticidal activity. The invention also provides compositions and combination products that contain a compound of the invention as active ingredient. Some of the combination products have shown synergistic activity against plant pathogens. The invention also provides fungicidal methods.

[0002] There is an acute need for new fungicides, because target pathogens are rapidly developing resistance to known fungicides. Widespread failure of N-substituted azole fungicides to control barley mildew was observed in 1983, and has been attributed to the development of resistance. The field performance of DMI (demethylation inhibitor) fungicides, which are now widely relied on to protect cereal crops from powdery mildew, has declined since they were introduced in the 1970's. Similarly, the pathogen population responsible for grape Botrytis, the number one disease in grapes as well as in berry crops and in tomato and cucumber greenhouse crops, has shifted to strains that are resistant to benzimidazole and dicarboximide fungicides.

[0003] The invention provides a fungicidal method which comprises applying to the locus of the fungus a fungicidally effective amount of a compound of the formula (1)



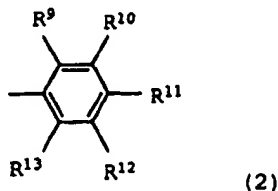
wherein

R¹ to R⁴ are one of the following:-

- a) R³ is Cl and R¹ and R⁴ are H;
- b) R³ is Br and R¹ and R⁴ are H;
- c) R¹ and R³ are Cl and R⁴ is H;
- d) R⁴ is Cl and R¹ and R³ are H;

A is

- a) (C₃-C₈) cycloalkyl or cycloalkenyl;
- b) a phenyl group of the formula (2)



wherein R⁹ to R¹³ are independently

H,
CN,
NO₂,
OH,
halo,

I,
 (C₁-C₄) alkyl,
 (C₃-C₄) branched alkyl,
 (C₂-C₄) acyl,
 halo (C₁-C₄) alkyl,
 hydroxy (C₁-C₄) alkyl,
 (C₁-C₄) alkoxy,
 halo (C₁-C₄) alkoxy,
 (C₁-C₄) alkylthio,
 halo (C₁-C₄) alkylthio,

an optionally substituted group phenyl-W-, where W is a bond, O,

[0004] SiR²⁰R²¹R²² or OSiR²⁰R²¹R²² where R²⁰, R²¹, and R²² are H, a C₁-C₆ alkyl group, straight chain or branched, phenyl or substituted phenyl, provided that at least one of R²⁰, R²¹, and R²² is other than H, or R¹¹ and R¹² or R¹² and R¹³ combine to form a carbocyclic ring, provided that unless all of the R⁹ to R¹³ are H or F, then at least two of R⁹ to R¹³ are H;

or an acid addition salt of a compound of formula (1), or an N-oxide of a compound of formula (1);

wherein the term "substituted" as used herein means substituted by up to three groups selected from halo, I, (C₁ to C₁₀) alkyl, branched (C₃-C₆) alkyl, halo (C₁-C₄) alkyl, hydroxy (C₁-C₄) alkyl, C₁-C₄ alkoxy, halo C₁-C₄ alkoxy, phenoxy, phenyl, NO₂, OH, CN (C₁-C₄) alkanoyloxy, or benzyloxy, but not including any such method for the therapeutic treatment of the human or animal body.

[0005] The invention also provides novel compounds of formula (1) as defined above provided that the following compounds are excluded:

- 1) compounds wherein R³ is Cl, R¹ and R⁴ are H, and A is phenyl, 4-chlorophenyl, or 4-fluorophenyl; and
- 2) 7-chloro-4-(3-trifluoromethyl)phenoxy)-quinoline;
- 3) 7-chloro-4-(4-chloro-3,5-dimethylphenoxy)-quinoline;
- 4) 7-chloro-4-(4-chloro-3-methylphenoxy)-quinoline;

[0006] The fungicidal combinations of the invention comprise at least 1% by weight of a compound of formula (1), or an acid addition salt of a compound of formula (1) or an N-oxide of a compound of formula (1) where Y is CH, in combination with a second fungicidal compound.

[0007] The fungicidal compositions of the invention comprise a compound of formula (1), or an acid addition salt of a compound of formula (1) or an N-oxide of a compound of formula (1) where Y is CH, in combination with a phyto-logically-acceptable carrier.

[0008] Various quinoline ethers and quinolinamines are known. In particular:-

[0009] JP 19548/68 and Derwent 66-33787 disclose 4-phenoxyquinolines having antimycotic activity.

[0010] H. Gildemeister et al., Leibigs Ann. Chem. 1982, 1656-76 at page 1660 discloses certain phenoxyquinoline compounds as intermediates in preparing bactericides and fungicides. The disclosed compounds include 4-(3-methyl-phenoxy)quinoline, 4-(3-methoxyphenoxy)quinoline, 6-fluoro-2-methyl-4-(2,6-dinitro-4-trifluoromethylphenoxy)quinoline, 6-methoxy-2-methyl-4-(2,6-dinitro-4-trifluoromethylphenoxy)quinoline, 2-methyl-7-trifluoromethyl-(2,6-dinitro-4-trifluoromethylphenoxy)quinoline, and 2-methyl-4-(4-nitrophenoxy)quinoline.

[0011] 53 Chem. Abst. 2229i (1959) discloses 4-(2,6-dinitro-4-methylphenoxy)quinoline N-oxide as having bacteriostatic properties.

[0012] 57 Chem. Abst. 16760e (1962) discloses a series of 2-methyl-quinolines that were tested for fungistatic activity.

[0013] 61 Chem. Abst. 5609h (1964) discloses a number of 2-methyl-4-phenoxyquinolines having various chlorine, methyl, and methoxy substitutions on the phenoxy ring. No utility is disclosed for the compounds.

[0014] 73 JACS 2623-26 (1951) discloses 7-chloro-4-phenoxyquinoline as an intermediate for antivirals.

[0015] 21 Eur. J. Med. Chem.-Chim. Ther., 5-8 (1986) discloses 4-(4-aminophenoxy)-7-chloroquinoline as a compound tested for antimalarial activity but found to be inactive.

[0016] US 3075981 discloses a number of 4-(substituted anilino) quinolines as intermediates.

[0017] Throughout this document, all temperatures are given in degrees Celsius, and all percentages are weight percentages unless otherwise stated.

[0018] The term halo, used alone or in combination with other terms, such as alkyl or alkoxy, refers to F, Cl, or Br.

[0019] The term "(C₁-C₄) alkyl" refers to straight chain alkyl radicals.

[0020] The term "branched (C₃-C₄) alkyl" refers to all alkyl isomers containing the designated number of carbon atoms, except the straight chain isomers.

[0021] The term "(C1-C4) alkoxy" refers to straight or branched chain alkoxy groups.

[0022] The term "halo (C1-C4) alkyl" refers to a (C1-C4) alkyl group, straight chain or branched, substituted with one or more halo atoms.

[0023] The term "halo (C1-C4) alkoxy" refers to a (C1-C4) alkoxy group, substituted with one or more halo atoms.

5 [0024] The term "halo (C1-C4) alkylthio" refers to a (C1-C4) alkylthio group, straight chain or branched, substituted with one or more halo groups.

[0025] The term "(C₁-C₄) acyl" refers to straight chain or branched acyl groups.

10 [0026] The term "substituted phenyl" refers to phenyl substituted with up to three groups selected from halo, I, (C₁-C₁₀) alkyl, branched (C₃-C₆) alkyl, halo (C₁-C₄) alkyl, hydroxy (C₁-C₄) alkyl, (C₁-C₄) alkoxy, halo (C₁-C₄) alkoxy, phenoxy, phenyl, NO₂, OH, CN, (C₁-C₄) alkanoyloxy, or benzyloxy.

[0027] The term "substituted phenoxy" refers to phenoxy substituted with up to three groups selected from halo, I, (C₁-C₁₀) alkyl, branched (C₃-C₆) alkyl, halo (C₁-C₄) alkyl, hydroxy (C₁-C₄) alkyl, (C₁-C₄) alkoxy, halo (C₁-C₄) alkoxy, phenoxy, phenyl, NO₂, OH, CN, (C₁-C₄) alkanoyloxy, or benzyloxy.

15 [0028] The term "substituted phenylthio" refers to a phenylthio group substituted with up to three groups selected from halo, I, (C₁-C₁₀) alkyl, branched (C₃-C₆) alkyl, halo (C₁-C₄) alkyl, hydroxy (C₁-C₄) alkyl, (C₁-C₄) alkoxy, halo (C₁-C₄) alkoxy, phenoxy, phenyl, NO₂, OH, CN, (C₁-C₄) alkanoyloxy, or benzyloxy.

[0029] The term "substituted phenylsulfonyl" refers to a phenylsulfonyl group substituted with up to three groups selected from halo, I, (C₁-C₁₀) alkyl, branched (C₃-C₆) alkyl, halo (C₁-C₄) alkyl, hydroxy (C₁-C₄) alkyl, (C₁-C₄) alkoxy, halo (C₁-C₄) alkoxy, phenoxy, phenyl, NO₂, OH, CN, (C₁-C₄) alkanoyloxy, or benzyloxy.

20 [0030] The term "unsaturated hydrocarbon chain" means a hydrocarbon chain containing one to three multiple bond sites.

[0031] The term "carbocyclic ring" refers to a saturated or unsaturated ring of four to seven carbon atoms.

[0032] "HPLC" refers to high-performance liquid chromatography.

25 Compounds

[0033] While all of the compounds of the invention are useful fungicides, certain classes are preferred for reasons of greater efficacy or ease of synthesis, viz:

- 30 1) Compounds of formula (1) where at least one of R¹, R³ and R⁴ is H;
 2) Compounds of preferred class (1) wherein two of R¹, R³ and R⁴ are hydrogen, and one is other than hydrogen;
 3) Compounds of preferred class 2 wherein R³ is Cl and R¹ and R⁴ are H;
 4) Compounds of preferred class 2 wherein R⁴ is Cl and R¹ and R³ are H.
 5) Compounds of preferred class 1 wherein R¹ and R³ are both Cl or both CH₃ and R⁴ is H;
 35 5a) Compounds of preferred class 5 wherein A is unsubstituted phenyl;
 6) Compounds of formula (1) wherein A is substituted phenyl;
 7) Compounds of preferred class 6 wherein R¹¹ is F;
 8) Compounds of preferred class 6 wherein A is phenyl ortho-substituted with an electron-withdrawing group;
 9) Compounds of preferred class 8 wherein R⁹ is halo, CF₃, CN, or NO₂;
 40 10) Compounds wherein A is 4-fluorophenyl;
 11) Compounds wherein A is phenyl ortho-substituted with an electron withdrawing group;

45 [0034] For curative as well as protective powdery mildew control, compounds of formula (1) wherein R³ is Cl (i.e., 7-chloro-4-quinolinyl ethers) are especially preferred, and most preferred within this class are 7-chloro-4-(4-fluorophenoxy)quinoline (a compound not claimed per se, but, included in the claimed methods and compositions), 7-chloro-4-(2-nitrophenoxy)-quinoline, 4-(2-bromophenoxy)-7-chloroquinoline, 7-chloro-4-(2-chlorophenoxy)quinoline, 2-[(7-chloro-4-quinolinyl)-oxy]benzonitrile, 7-chloro-4-(2,4-difluorophenoxy)quinoline, 7-chloro-4-(2-cyanophenoxy)quinoline, and 7-chloro-4-[2-(trifluoromethyl)phenoxy]quinoline.

50 [0035] For protective, as well as some curative powdery mildew control, compounds of formula (1) wherein R¹ and R³ are Cl (i.e., 5,7-dichloro-4-quinolinyl ethers) are especially preferred. Most preferred within this class are 5,7-dichloro-4-(4-fluorophenoxy)quinoline, 5,7-dichloro-4-(4-fluorophenoxy)-quinoline, hydrochloride, 5,7-dichloro-4-(phenoxy)-quinoline, and 5,7-dichloro-4-(4-fluorophenoxy)quinoline, 1-oxide.

[0036] Another preferred compound for control of powdery mildew is 7-chloro-4-[(4-fluorophenyl)methyl]quinoline.

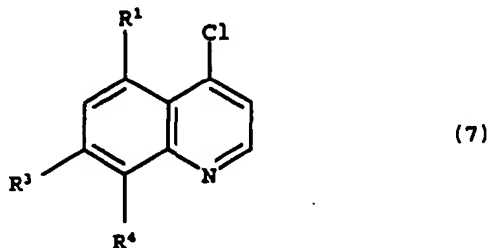
55 [0037] For activity against Botrytis, compounds of formula (1) wherein R⁴ is C1 (i.e., 8-chloro-4-quinolinyl ethers) are especially preferred. Most preferred within this class are 8-chloro-4-(2-chlorophenoxy)quinoline, 8-chloro-4-(2-chloro-4-fluoro-phenoxy)quinoline, and 4-(2-bromophenoxy)-8-chloroquinoline.

[0038] Although powdery mildew and Botrytis have been mentioned as being of particular interest, the data presented hereinafter will demonstrate that the compounds of the invention control many other plant pathogens as well.

Synthesis

[0039] The compounds of this invention are made using well known chemical procedures. The required starting materials are commercially available, or they are readily synthesized using standard procedures.

[0040] The compounds of formula (1) can be made by condensing a compound of formula (7) :



wherein R¹ to R³ and R⁴ are as previously defined, with a compound of the formula (8)



where

A is as previously defined.

[0041] The reaction can be carried out neat, at a temperature in the range of 80 to 150°C, preferably 130 to 140°C. An excess of the compound of formula (8) for example a two-fold excess, is typically used. Reaction time is typically two to 48 hours. The starting compound of formula (8) is then removed by diluting the reaction mixture with ethyl acetate, and washing with aqueous NaOH. Drying the organic layer over MgSO₄, and reducing pressure to remove solvent delivers the product.

[0042] In a preferred procedure, the chloride of formula (7) is reacted overnight with 1.2 to 1.4 equivalents of starting material of formula (8) in xylene at reflux.

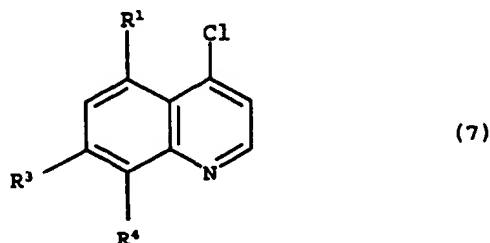
Derivatives

[0043] N-oxides of the compounds of formula (1) are prepared by reacting the compound of formula (1) with an oxidizing agent, such as 3-chloroperoxybenzoic acid or hydrogen peroxide, in a non-reactive organic solvent, such as methylene chloride or chloroform, at -20°C to room temperature, preferably at about 0°C.

[0044] The acid addition salts of compounds of formula (1) are obtained in the usual way.

[0045] Thus, the invention also provides a process for preparing a compound of formula (1) which comprises

(a) condensing a compound of formula (7)



wherein R¹, R³ and R⁴ are as defined in formula (1) with a compound of formula (8)

where A is as defined in formula (1) to provide a compound of formula (1)

Starting Materials

[0046] Phenol starting materials of formula (8) are commercially available or can be synthesized from the corresponding aniline via the Bucherer reaction, in which the aniline is reacted with aqueous sodium bisulfite. *Ang. Chem. Int. Ed. Eng.* 6, 307, 1967.

[0047] In the case of *ortho*-hydroxy-benzotrifluoride, a preferred preparation method is to react *ortho*-chlorobenzotrifluoride with sodium benzyolate. The resulting ether is then hydrogenolyzed to provide the desired product.

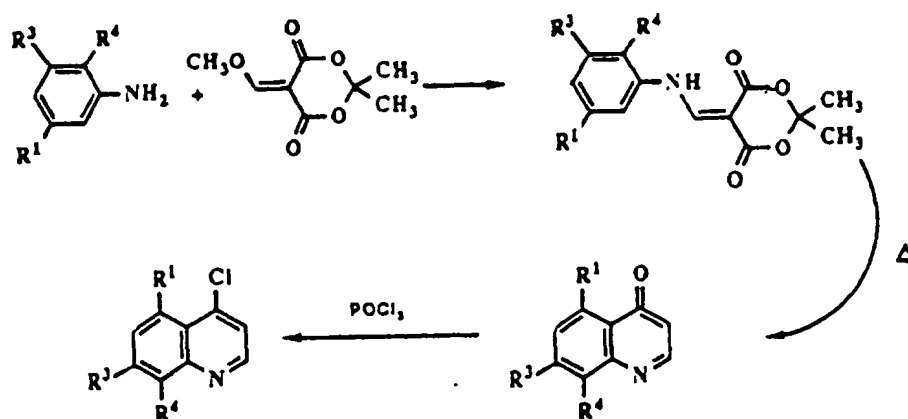
[0048] Thiol starting materials of formula (9) are similarly commercially available or are synthesized using conventional procedures.

Preparation of Quinoline Starting Materials

[0049] Quinoline starting materials can be synthesized using a variety of known procedures.

[0050] *Organic Syntheses*, collective volume 3, 1955, pp. 272-75, gives a procedure for preparing 4,7-dichloroquinoline, and other polysubstituted quinolines. Another general procedure is described in *Tetrahedron*, vol. 41, pp. 3033-36 (1985).

[0051] Many of the quinoline starting materials used in the following examples were prepared as shown in the following reaction scheme



In cases where mixtures of isomeric products were obtained, the mixture of substituted 4-quinolones was chlorinated under standard conditions, and the isomeric 4-chloroquinolines were separated by liquid chromatography.

[0052] 4,5-dichloroquinoline was prepared by reacting 3-chloroaniline with acrylic acid in water at ambient temperature for two days. The crude product was then isolated and heated to 100°C in solution with an excess of polyphosphoric acid, thereby furnishing a mixture of 5- and 7-chlorotetrahydroquinolin-4-ones. Chromatographic separation of the 5-chloro analog, followed by treatment with iodine in hot glacial acetic acid provided 4-hydroxy-5-chloroquinoline, which was halogenated to provide the desired intermediate. French Patent Number 1514280.

[0053] Other 4-chloro-5-substituted quinolines were prepared by converting the corresponding 5-substituted quinoline to the N-oxide, chlorinating, and separating the resulting mixture of 4-chloro and 2-chloro isomers using HPLC.

[0054] The 5-fluoro and 5-bromo quinolines can be prepared using the same general procedure. *J.A.C.S.*, vol. 71, 1785 (1949). The bromo-quinolines can then be lithiated and quenched with suitable electrophiles at low temperatures to provide other 5-substituted quinolines. *Chem. Ber.*, vol. 696, pp. 98 (1966).

[0055] Preparation of nitroquinolines is disclosed in *J.A.C.S.*, vol. 68, pp. 1267 (1946). Nitration of 4-chloroquinoline proceeds cleanly to deliver a mixture of 5- and 8-nitro-4-chloroquinolines, which can be separated by liquid chromatography. The 6- and 7-nitro compounds can be made via decarboxylation of the silver salts of the appropriate nitroquinoline-3-carboxylic acid.

EXAMPLES

[0056] The following examples are compounds actually prepared by the above described general procedures. The melting point is given for each compound. Specific illustrative preparations for the compounds of Examples 2, 15, 17, 23, 26 and 30 follow the tabular listing.

TABLE 1

| 4-(Aryloxy)quinolines | | |
|-----------------------|---|-----------|
| EXAMPLE NUMBER | COMPOUND | M.P. |
| 1* | 7-chloro-4-[3-(trifluoromethyl)phenoxy]quinoline | 96-97°C |
| 2* | 7-chloro-4-(4-fluorophenoxy)quinoline | 94°C |
| 3* | 7-chloro-4-(4-chlorophenoxy)quinoline | 82°C |
| 4 | 2-[(7-chloro-4-quinolinyl)oxy]benzonitrile | 122-123°C |
| 5* | 7-chloro-4-phenoxyquinoline | 44-46°C |
| 6* | 7-chloro-4-(4-fluorophenoxy)quinoline, 1-oxide | 164-165°C |
| 7 | 7-chloro-4-(3-chlorophenoxy)quinoline | 99-101°C |
| 8 | 4-(2-bromophenoxy)-7-chloroquinoline | 71-73°C |
| 9 | 7-chloro-4-(2,4-difluorophenoxy)quinoline | 116-118°C |
| 10 | 7-chloro-4-(2,3,5,6-tetrafluorophenoxy)quinoline | 121-123°C |
| 11 | 7-fluoro-4-(4-fluorophenoxy)quinoline | 76-77°C |
| 12 | 7-chloro-4-(2-chlorophenoxy)quinoline | 69-70°C |
| 13 | 7-chloro-4-(2,6-difluorophenoxy)quinoline | 134-136°C |
| 14 | 5,7-dichloro-4-(4-fluorophenoxy)quinoline, 1-oxide | 139-140°C |
| 15 | 7-chloro-4-(2-chloro-4-fluorophenoxy)quinoline, 1-oxide | 177-178°C |
| 16 | 5,7-dichloro-4-(4-fluorophenoxy)quinoline | 213-220°C |
| 17 | 7-chloro-4-(4-fluorophenoxy)quinoline, hydrochloride | 221-224°C |
| 18 | 8-bromo-4-(2-chlorophenoxy)quinoline | 68-71°C |
| 19 | 7-chloro-4-[2-(i-propyl)phenoxy]quinoline | oil |
| 20 | 4-(4-fluorophenoxy)-5,7-dimethylquinoline | 92-94°C |
| 21 | 7-chloro-4-(pentafluorophenoxy)quinoline | 95°C |

*a compound not claimed per se

TABLE 1 (continued)

| 4-(Aryloxy)quinolines | | |
|-----------------------|--|-----------|
| EXAMPLE NUMBER | COMPOUND | M.P. |
| 22 | 7-chloro-4-(3-chloro-4-fluorophenoxy)quinoline | 124-127°C |
| 23 | 5,7-dichloro-4-(4-fluorophenoxy)quinoline | 82°C |
| 24 | 7-chloro-4-(4-phenoxyphenoxy)quinoline | 54-55°C |
| 25 | 7-chloro-4-[4-(t-butyl)phenoxy]quinoline | 144-145°C |
| 26 | 8-chloro-4-(2-chlorophenoxy)quinoline | 56-58°C |
| 27 | 8-chloro-4-[2-(trifluoromethyl)phenoxy]quinoline | 64-66°C |
| 28 | 4-(2-bromophenoxy)-8-chloroquinoline | 70-72°C |
| 29 | 8-chloro-4-(2-fluorophenoxy)quinoline | 60-62°C |
| 30 | 8-chloro-4-(2-chloro-4-fluorophenoxy)quinoline | 99-101°C |
| 31 | 5,1-dichloro-4-(2,4-difluorophenoxy)quinoline | 110-111°C |
| 32 | 5,7-dichloro-4-(2-nitrophenoxy)quinoline | 84-86°C |
| 33 | 5,1-dichloro-4-[2-(trifluoromethyl)phenoxy]quinoline | 86-89°C |
| 34 | 8-chloro-4-(4-fluorophenoxy)-5-methylquinoline | 105-106°C |
| 35 | 7-chloro-4-[4-(i-propyl)phenoxy]quinoline | 52-55°C |
| 36 | 8-chloro-4-[4-(i-propyl)phenoxy]quinoline | 101-103°C |
| 37 | 7-chloro-4-(3-fluorophenoxy)quinoline | 71-73°C |
| 38 | 7-chloro-4-(2-fluorophenoxy)quinoline | 72-73°C |
| 39 | 7-chloro-4-(4-methylphenoxy)quinoline | 78-80°C |
| 40 | 7-chloro-4-(4-methoxyphenoxy)quinoline | 88-90°C |
| 41 | 7-chloro-4-(2-methoxyphenoxy)quinoline | 81-83°C |
| 42 | 7-chloro-4-(2-methylphenoxy)quinoline | 48-50°C |
| 43 | 7-chloro-4-(3-nitrophenoxy)quinoline | 149-151°C |
| 44 | 7-chloro-4-(2-nitrophenoxy)quinoline | 113-115°C |
| 45 | 7-chloro-4-(4-nitrophenoxy)quinoline | 157-159°C |

TABLE 1 (continued)

| 4-(Aryloxy)quinolines | | |
|-----------------------|--|-----------|
| EXAMPLE NUMBER | COMPOUND | M.P. |
| 46 | 7-chloro-4-[2-(trifluoromethyl)phenoxy]quinoline | 59-61°C |
| 47 | 7-chloro-4-[4-(trifluoromethyl)phenoxy]quinoline | 81-82°C |
| 48 | 4-(2-bromo-4-fluorophenoxy)-7-chloroquinoline | 100-102°C |
| 49 | 8-chloro-4-(2,4-dichlorophenoxy)quinoline | 165-167°C |
| 50 | 8-chloro-4-(2-cyanophenoxy)quinoline | 119-121°C |
| 51 | 8-chloro-4-(2-iodophenoxy)quinoline | oil |
| 52 | 7-chloro-4-(2,6-dibromo-4-fluorophenoxy) | 128-130°C |
| 53 | 7-chloro-4-[3-(t-butyl)phenoxy]quinoline | oil |
| 54 | 7-chloro-4-[2-(t-butyl)phenoxy]quinoline | 90-92°C |
| 55 | 4-[(7-chloro-4-quinolinyl)oxy]phenol | 211-213°C |
| 56 | 2-[(7-chloro-4-quinolinyl)oxy]phenol | 209-211°C |
| 57 | 4-([1,1'-biphenyl]-2-yloxy)-7-chloroquinoline | oil |
| 58 | 7-chloro-4-(2-chloro-4-fluorophenoxy)quinoline | 86-89°C |
| 59 | 7-chloro-4-(2-iodophenoxy)quinoline | 68-70°C |
| 60 | 8-fluoro-4-(4-fluorophenoxy)quinoline | 85-87°C |
| 61 | 7-bromo-4-(4-fluorophenoxy)quinoline | 87-89°C |
| 62 | 7-bromo-4-(2,4-difluorophenoxy)quinoline | 110-112°C |
| 63 | 5,7-dichloro-4-(2-fluorophenoxy)quinoline | 99-101°C |
| 64 | 5,7-dichloro-4-(2-chlorophenoxy)quinoline | 78-79°C |
| 65 | 5,7-dichloro-4-(2-cyanophenoxy)quinoline | 88-90°C |
| 66 | 5,7-dichloro-4-(2-chloro-4-fluorophenoxy)quinoline | 83-85°C |
| 67 | 8-chloro-4-(2,4-difluorophenoxy)quinoline | 105-107°C |
| 68 | 8-chloro-4-(3-chloro-2-nophenoxy)quinoline | 86-88°C |
| 69 | 4-(2-bromo-4-fluorophenoxy)-8-chloroquinoline | 106-107°C |

EP 0 326 330 B1

TABLE 1 (continued)

| 4-(Aryloxy)quinolines | | |
|-----------------------|--|-----------|
| EXAMPLE NUMBER | COMPOUND | M.P. |
| 70 | 8-chloro-4-(3-chlorophenoxy)quinoline | 82-84°C |
| 71 | 7-chloro-4-[4-[(trifluoromethyl)thio]phenoxy]quinoline | 90-91°C |
| 72 | 4-(3-chloro-4-fluorophenoxy)-8-chloroquinoline | 88-90°C |
| 73 | 8-chloro-4-(2-methylphenoxy)quinoline | 85-87°C |
| 74 | 8-chloro-4-(2,6-dichlorophenoxy)quinoline | 156-159°C |
| 75 | 8-chloro-4-(2-methoxyphenoxy)quinoline | 120-122°C |
| 76 | 8-chloro-4-(4-methoxyphenoxy)quinoline | 119-121°C |

TABLE 2

| Additional Compounds | | |
|----------------------|---|-----------|
| EXAMPLE NUMBER | COMPOUND | M.P. |
| 77* | 7-chloro-4-(4-chloro-3,5-dimethylphenoxy)quinoline | 102°C |
| 78* | 7-chloro-4-(4-chloro-3-methylphenoxy)quinoline | 85°C |
| 79* | 5-chloro-4-[2,6-dinitro-4-(trifluoromethyl)phenoxy]-2,8-dimethylquinoline | 189°C |
| 80* | 8-chloro-2-methyl-4-[2-nitro-4-(trifluoromethyl)phenoxy]quinoline | 184°C |
| 81 | 7-chloro-4-(3-methylphenoxy)quinoline | 77-79°C |
| 82 | 4-[(7-chloro-4-quinolinyloxy)benzonitrile | 142-144°C |
| 83 | 3-[(7-chloro-4-quinolinyloxy)beazonitrile | 133-134°C |
| 84 | 4-(4-bromophenoxy)-7-chloroquinoline | 82-84°C |
| 85 | 7-chloro-4-(4-iodophenoxy)quinoline | 110-113°C |
| 86 | 4-(3-bromophenoxy)-7-chloroquinoline | 89-91°C |
| 87 | 7-chloro-4-(4-fluorophenoxy)-6-methoxyquinoline | 123-125°C |
| 88 | 8-chloro-4-(2,4-dichloro-6-fluorophenoxy)quinoline | 90-92°C |
| 89 | 8-chloro-4-(2-ethoxyphenoxy)quinoline | 76-78°C |
| 90 | 8-chloro-4-(4-fluoro-2-methylphenoxy)quinoline | 103-105°C |

*a compound not claimed per se

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TABLE 2 (continued)

| Additional Compounds | | |
|----------------------|--|-----------|
| EXAMPLE NUMBER | COMPOUND | M.P. |
| 91 | 7-chloro-4-(2-methyl-4-fluorophenoxy)quinoline | 98-100°C |
| 92 | 8-chloro-4-(4-chloro-2-fluorophenoxy)quinoline | 142-144°C |
| 93 | 4-(2,6-dibromo-4-nitrophenoxy)-8-chloroquinoline | 232-233°C |
| 94 | 4-(4-bromo-2-fluorophenoxy)-8-chloroquinoline | 122-125°C |
| 95 | 8-chloro-4-(2,4-dibromophenoxy)quinoline | 115-116°C |
| 96 | 8-chloro-4-(4-fluoro-2-nitrophenoxy)quinoline | 133-135°C |
| 97 | 8-chloro-4-(2,4,6-trichlorophenoxy)quinoline | 153-155°C |
| 98 | 7-chloro-4-(4-fluorophenoxy)-2-methylquinoline | 141-142°C |
| 99 | 8-chloro-4-(2-nitrophenoxy)quinoline | 142-144°C |
| 100 | 5,7-dichloro-4-(3-bromophenoxy) quinoline | 120-121°C |
| 101 | 8-bromo-4-(4-fluorophenoxy)quinoline | 122-123°C |
| 102 | 5,7-dichloro-4-(4-fluorophenoxy)-6-methylquinoline | 110-112°C |
| 103 | 7-chloro-4-(2,4-dinitrophenoxy)quinoline | 181-183°C |
| 104 | 8-chloro-4-(2,6-dibromo-4-fluorophenoxy)quinoline | 195-197°C |
| 105 | 5-chloro-2,8-dimethyl-4-(4-fluorophenoxy)quinoline | 75-76°C |
| 106 | 8-chloro-4-(3-methylphenoxy)quinoline | 46-48°C |
| 107 | 7-chloro-4-[2-(methylthio)phenoxy]quinoline | 107-108°C |
| 108 | 7-chloro-4-(4-ethoxyphenoxy)quinoline | 113-115°C |
| 109 | 8-chloro-4-(4-ethoxyphenoxy)quinoline | 94-96°C |
| 110 | 5,7-dichloro-4-phenoxyquinoline | 97-99°C |
| 111 | 7-chloro-4-(3-methoxyphenoxy)quinoline | 69-70°C |
| 112 | 8-chloro-4-(4-iodophenoxy)quinoline | 114-116°C |
| 113 | 8-chloro-4-(4-chloro-2-methylphenoxy)quinoline | 143-145°C |
| 114 | 4-(4-chloro-3,5-dimethylphenoxy)-8-chloroquinoline | 128-129°C |

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TABLE 2 (continued)

| Additional Compounds | | |
|----------------------|---|-----------|
| EXAMPLE NUMBER | COMPOUND | M.P. |
| 115 | 4-(4-chloro-2-nitrophenoxy)-8-chloroquinoline | 149-150°C |
| 116 | 8-chloro-4-(2-ethylphenoxy)quinoline | oil |
| 117 | 4-[(1,1'-biphenyl)-4-yloxy]-7-chloroquinoline | 139-141°C |
| 118 | 3-[(7-chloro-4-quinolinyl)oxy]phenol | 150-154°C |
| 119 | 7-chloro-4-(2-phenoxyphenoxy)quinoline | 84-86°C |
| 120 | 8-chloro-4-(2-chlorophenoxy)quinazoline | 127-129°C |
| 121 | 8-chloro-4-(2-chloro-4-fluorophenoxy)quinazoline | 172-173°C |
| 122 | 8-chloro-4-[2-(methylthio)phenoxy]quinoline | 67-69°C |
| 123 | 8-chloro-4-(4-methylphenoxy)quinoline | 97-98°C |
| 124 | 8-chloro-4-(2,3-dimethylphenoxy)quinoline | 118-120°C |
| 125 | 8-chloro-4-(3,4-dimethylphenoxy)quinoline | 88-90°C |
| 126 | 7-chloro-4-[4-(trifluoromethoxy)phenoxy]quinoline | 79-80°C |
| 127 | 8-chloro-4-[4-(trifluoromethoxy)phenoxy]quinoline | 131-133°C |
| 128 | 8-chloro-4-(2,5-dichlorophenoxy)quinoline | 70-73°C |
| 129 | 8-chloro-4-(2,6-dimethylphenoxy)quinoline | 125-127°V |
| 130 | 8-chloro-4-(3,5-dimethylphenoxy)quinoline | 85-87°C |
| 131 | 8-chloro-4-(2-chloro-6-methylphenoxy)quinoline | 154-156°C |
| 132 | 8-chloro-4-(2,5-dimethylphenoxy)quinoline | 51-53°C |
| 133 | 8-chloro-4-[2-chloro-5-(trifluoromethyl)phenoxy]quinoline | 120-122°C |
| 134 | 4-(2-chloro-4-nitrophenoxy)-8-chloroquinoline | 179-181°C |
| 135 | 4-(2,4-dibromophenoxy)-7-chloroquinoline | 134-136°C |
| 136 | 4-(4-bromo-2-fluorophenoxy)-7-chloroquinoline | 129-131°C |
| 137 | 8-chloro-4-(4-ethylphenoxy)quinoline | 70-72°C |
| 138 | 7-chloro-4-(2,6-dimethylphenoxy)quinoline | 54-56°C |

TABLE 2 (continued)

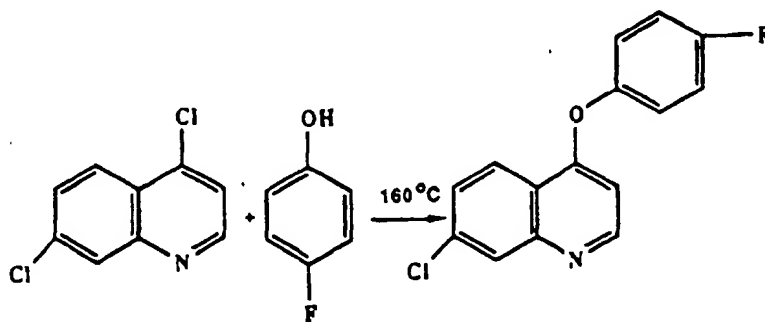
| Additional Compounds | | |
|----------------------|--|-----------|
| EXAMPLE NUMBER | COMPOUND | M.P. |
| 139 | 8-fluoro-4-(2-phenylphenoxy)quinoline | N/A |
| 140 | 4-(2-chloro-4,6-difluorophenoxy)-8-chloroquinoline | 99-101°C |
| 141 | 8-chloro-4-[(1-methylcyclopentyl)oxy]quinoline | 82-83°C |
| 142 | 4-[(5,7-dichloro-4-quinolinyloxy]benzotrile | 161-163°C |
| 143 | 3-bromo-7-chloro-4-(2,4-difluorophenoxy)quinoline | 113-114°C |
| 144 | 3-bromo-7-chloro-4-(4-fluorophenoxy)quinoline | 96.5-98°C |
| 145 | 3-bromo-4-(2-chloro-4-fluorophenoxy)-7-chloroquinoline | 140-141°C |
| 146 | 3-bromo-4-(2-chlorophenoxy)-7-chloroquinoline | 146-148°C |
| 147 | 3-bromo-4-(2-bromo-4-fluorophenoxy)-7-chloroquinoline | 152-154°C |

[0057] The following detailed descriptions of the procedures used to prepare selected examples are representative of the procedures used to prepare the compounds of the other examples.

Examples 2 and 17

7-Chloro-4-(4-fluorophenoxy)quinoline and 7-Chloro-4-(4-fluorophenoxy)quinoline, hydrochloride

[0058]



A slurry comprising 7.92 g (.04 mol) of 4,7-dichloroquinoline, 4.48 g (.04 mol) of 4-fluorophenol, and 24 ml of xylene was stirred and heated to reflux. The resulting clear orange solution was refluxed at 144°C for 17 hours, at which time an additional 0.90 g (.008 mol) of 4-fluorophenol was added, and refluxing was continued. The mixture was concentrated to a brown solid, which was dissolved in a mixture of CH_2Cl_2 (50 ml) and 1N NaOH (50 ml). The organic layer was washed four times with 50 ml of 1N NaOH, then dried with Na_2SO_4 , and concentrated to a brown oil (9.8 g), which crystallized. The product, 7-chloro-4-(4-fluorophenoxy)quinoline, was recrystallized from hexane, yielding a white crystalline solid. Yield: 8.01 g (73.2%). M.P. 91-92°C.

[0059] The corresponding amine hydrochloride, was prepared using a similar procedure, except that after refluxing the reaction mixture for 18 hours, the mixture was cooled to room temperature, and anhydrous HCl was added over

one half hour period. The mixture was then cooled to 0°C and held at 0°C for two hours. The mixture was then filtered and the product dried under vacuum at 40°C. The filtrate was stirred 48 hours at room temperature, during which time additional product precipitated. The product, 7-chloro-4-(4-fluorophenoxy)quinoline, hydrochloride, was recrystallized from 40 ml propanol. Yield: 9.10 g (73%). M.P. 220-224°C.

Example 15

7-Chloro-4-(2-chloro-4-fluorophenoxy)quinoline, 1-oxide

[0060] A mixture of 5.0 g (16.22 mmol) of 4-(2-chloro-4-fluorophenoxy)-7-chloroquinoline, 4.20 g (19.47 mmol) of 80% 3-chloroperoxybenzoic acid, and 50 ml of CH₂Cl₂ was stirred at 0°C for six hours. The CH₂Cl₂ was removed by reducing pressure, and the residue was dissolved in ethyl acetate and washed with base. After removing solvent from the organic layer by reducing pressure, a white solid formed. This was recrystallized in ethyl acetate. Yield 3.04 g (58%). M.P. 177-178°C.

| Analysis: | | | |
|-----------|-----------|----------|----------|
| Theory | C, 55.58; | H, 2.49; | N, 4.32; |
| Found | C, 55.67; | H, 2.46; | N, 4.43. |

Example 23

5,7-Dichloro-4-(4-fluorophenoxy)quinoline

[0061] A mixture of 29.11 g of 4,5,7-trichloroquinoline and 16.84 g of 4-fluorophenol was heated to 160°C. After approximately 40 minutes, the molten solution solidified. The solid was dissolved in ethyl acetate and 2N NaOH. The organic layer was washed with base to remove excess phenol, then dried. Solvent was removed by reducing pressure, and the residue was purified by recrystallizing in heptane to produce 29.49 g of the title product. M.P. 105-106°C.

| Analysis: | | | |
|-----------|-----------|----------|----------|
| Theory | C, 58.47; | H, 2.62; | N, 4.55; |
| Found | C, 58.38; | H, 2.52; | N, 4.55. |

Example 26

8-chloro-4-(2-chlorophenoxy)quinoline

[0062] A mixture of 2.0 g of 4,8-dichloroquinoline and 2.6 g of 2-chlorophenol was heated to 160°C and stirred. Progress of the reaction was monitored by TLC. When no 4,8-dichloroquinoline remained, the reaction mixture was diluted with ethyl acetate, and washed with base to remove most of the excess phenol. To remove phenol remaining after washing, the product was purified using HPLC. Fractions containing product were combined, and solvent was removed using reduced pressure. The oily product crystallized. Yield: 1.36 g (46%). M.P. 56-58°C.

| Analysis: | | | |
|-----------|-----------|----------|----------|
| Theory | C, 62.09; | H, 3.13; | N, 4.83; |
| Found | C, 62.14; | H, 3.11; | N, 5.04. |

Example 30

8-chloro-4-(2-chloro-4-fluorophenoxy)quinoline

[0063] A mixture of 2.0 g of 4,8-dichloroquinoline and 2.96 g of 2-chloro-4-fluorophenol was heated to 160°C and stirred. Progress of the reaction was monitored using TLC. When no 4,8-dichloroquinoline remained, the product was washed with base to remove phenol, then purified using HPLC. A brown solid resulted, which was recrystallized in heptane to give 1.54 g of the title product as yellow crystals. Yield: 49%. M.P. 99-101°C.

| Analysis: | | | |
|-----------|-----------|----------|----------|
| Theory | C, 58.47; | H, 2.62; | N, 4.55; |
| Found | C, 58.39; | H, 2.85; | N, 4.49. |

Utility

[0064] The compounds of formula (1) have been found to control fungi, particularly plant pathogens. When employed in the treatment of plant fungal diseases, the compounds are applied to the plants in a disease inhibiting and phyto-logically acceptable amount. The term "disease inhibiting and phytologically acceptable amount," as used herein, refers to an amount of a compound of the invention which kills or inhibits the plant disease for which control is desired, but is not significantly toxic to the plant. This amount will generally be from about 1 to 1000 ppm, with 10 to 500 ppm being preferred. The exact concentration of compound required varies with the fungal disease to be controlled, the type formulation employed, the method of application, the particular plant species, climate conditions and the like. The compounds of the invention may also be used to protect stored grain and other non-plant loci from fungal infestation.

Greenhouse Tests

[0065] The following experiments were performed in the laboratory to determine the fungicidal efficacy of the compounds of the invention.

Test 1

[0066] This screen was used to evaluate the efficacy of the present compounds against a variety of different organisms that cause plant diseases.

[0067] The test compounds were formulated for application by dissolving 50 mg of the compound in 1.25 ml of solvent. The solvent was prepared by mixing 50 ml of "Tween 20" (polyoxyethylene (20) sorbitan monolaurate surfactant) with 475 ml of acetone and 475 ml of ethanol. The solvent/compound solution was diluted to 125 ml with deionized water. The resulting formulation contains 400 ppm test chemical. Lower concentrations were obtained by serial dilution with the solvent-surfactant mixture.

[0068] The formulated test compounds were applied by foliar spray. The following plant pathogens and their corresponding plants were employed.

| Pathogen | Designation in Following Tables | Host |
|--|---------------------------------|----------------|
| <u>Erysiphe graminis tritici</u> (powdery mildew) | POWD MDEW | wheat |
| <u>Pyricularia oryzae</u> (rice blast) | RICE BLAS | rice |
| <u>Puccinia recondita tritici</u> (leaf rust) | LEAF RUST | wheat |
| <u>Botrytis cinerea</u> (gray mold) | GRAY MOLD | grape berries |
| <u>Pseudoperonospora cubensis</u> (downy mildew) | DOWN MDEW | squash |
| <u>Cercospora beticola</u> (leaf spot) | LEAF SPOT | sugar beet |
| <u>Venturia inaequalis</u> (apple scab) | APPL SCAB | apple seedling |

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(continued)

| Pathogen | Designation in Following Tables | Host |
|--|---------------------------------|-------|
| <u>Septoria tritici</u> (leaf blotch) | LEAF BLOT | wheat |

The formulated technical compounds were sprayed on all foliar surfaces of the host plants (or cut berry) to past run-off. Single pots of each host plant were placed on raised, revolving pedestals in a fume hood. Test solutions were sprayed on all foliar surfaces. All treatments were allowed to dry and the plants were inoculated with the appropriate pathogens within 2-4 hours.

[0069] The effectiveness of test compounds in controlling disease was rated using the following scale:

- 0 = not tested against specific organism
- = 0-19% control at 400 ppm
- + = 20-89% control at 400 ppm
- ++ = 90-100% control at 400 ppm
- +++ = 90-100% control at 100 ppm

Results are reported in the following Table 7:

TABLE 7

| COMPOUND EX NO. | POWD MDEW | RICE BLAS | LEAF RUST | GRAY MOLD | DOWN MDEW | LEAF SPOT | APPL SCAB | LEAF BLOT |
|--------------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| 1 | + | - | - | - | - | - | - | + |
| 2 | +++ | - | - | - | + | 0 | - | + |
| 3 | ++ | - | - | - | + | 0 | - | + |
| 4 | +++ | - | - | - | - | - | - | - |
| 5 | ++ | + | + | - | - | + | - | - |
| 6 | +++ | - | + | - | + | ++ | - | + |
| 7 | ++ | - | - | - | - | - | - | - |
| 8 | +++ | - | - | - | + | - | - | + |
| 9 | +++ | - | - | - | - | + | - | - |
| 10 | + | - | + | - | + | + | - | + |
| 11 | + | - | + | - | ++ | - | - | - |
| 12 | +++ | - | + | - | - | - | - | - |
| 13 | ++ | - | - | - | + | - | - | - |
| 14 | +++ | + | - | - | - | + | - | - |
| 15 | ++ | - | - | - | ++ | + | - | + |
| 16 | +++ | - | - | - | + | 0 | 0 | 0 |
| 17 | +++ | - | - | - | - | 0 | 0 | 0 |
| 18 | +++ | ++ | - | ++ | ++ | 0 | 0 | 0 |
| 19 | ++ | ++ | - | + | + | 0 | 0 | 0 |
| 20 | +++ | ++ | ++ | - | - | 0 | 0 | 0 |
| 21 | + | - | - | - | - | - | - | - |
| 22 | + | - | - | - | - | 0 | 0 | 0 |
| 23 | +++ | - | + | - | - | + | - | - |
| 24 | +++ | + | - | - | + | - | - | - |
| 25 | + | - | + | - | - | 0 | 0 | 0 |
| 26 | + | ++ | + | +++ | ++ | + | +++ | - |
| 27 | + | + | - | - | - | - | - | + |
| 28 | + | + | - | +++ | + | - | + | - |
| 29 | + | - | - | + | - | 0 | 0 | 0 |

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TABLE 7 (continued)

| | COMPOUND EX NO. | POWD MDEW | RICE BLAS | LEAF RUST | GRAY MOLD | DOWN MDEW | LEAF SPOT | APPL SCAB | LEAF BLOT |
|----|--------------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| 5 | 30 | + | - | + | +++ | + | - | +++ | + |
| | 31 | +++ | - | - | - | - | 0 | 0 | 0 |
| | 32 | + | + | - | - | ++ | 0 | 0 | 0 |
| | 33 | ++ | + | - | - | - | 0 | 0 | 0 |
| | 34 | ++ | - | - | - | - | 0 | 0 | 0 |
| 10 | 35 | + | - | - | - | - | 0 | 0 | 0 |
| | 36 | - | - | - | + | - | 0 | 0 | 0 |
| | 37 | ++ | + | - | - | - | - | - | + |
| | 38 | +++ | - | - | - | - | + | - | + |
| 15 | 39 | + | - | - | - | - | 0 | 0 | 0 |
| | 40 | ++ | - | + | - | + | - | - | - |
| | 41 | + | - | + | - | ++ | - | + | - |
| | 42 | + | + | - | - | + | - | - | - |
| | 43 | + | - | - | - | - | - | - | - |
| 20 | 44 | ++ | - | - | - | - | - | - | + |
| | 45 | ++ | + | - | - | - | - | - | - |
| | 46 | +++ | + | - | - | + | - | - | - |
| | 47 | + | - | - | - | + | 0 | 0 | 0 |
| | 48 | +++ | + | + | - | - | 0 | 0 | 0 |
| 25 | 49 | + | - | - | - | - | 0 | 0 | 0 |
| | 50 | + | + | - | - | + | 0 | 0 | 0 |
| | 51 | ++ | ++ | + | ++ | + | 0 | 0 | 0 |
| | 52 | + | - | - | - | - | 0 | 0 | 0 |
| 30 | 53 | ++ | + | + | - | + | - | - | + |
| | 54 | ++ | + | - | - | - | - | - | + |
| | 55 | - | - | + | - | + | 0 | 0 | 0 |
| | 56 | - | - | - | - | - | 0 | 0 | 0 |
| 35 | 57 | + | + | - | - | + | - | - | + |
| | 58 | ++ | - | - | - | - | - | - | + |
| | 59 | +++ | - | + | - | - | - | - | + |
| | 60 | - | + | + | + | ++ | - | + | + |
| | 61 | +++ | + | + | - | - | 0 | 0 | 0 |
| 40 | 62 | +++ | - | - | - | - | 0 | 0 | 0 |
| | 63 | + | - | - | - | - | 0 | 0 | 0 |
| | 64 | +++ | - | - | - | - | - | - | + |
| | 65 | + | ++ | - | - | + | - | - | + |
| 45 | 66 | +++ | - | - | - | + | - | - | - |
| | 67 | + | + | - | ++ | ++ | 0 | 0 | 0 |
| | 68 | - | ++ | + | ++ | + | 0 | 0 | 0 |
| | 69 | + | + | - | ++ | + | 0 | 0 | 0 |
| | 70 | + | - | + | + | - | 0 | 0 | 0 |
| 50 | 71 | ++ | - | - | - | - | 0 | 0 | 0 |
| | 72 | - | - | + | ++ | + | 0 | 0 | 0 |
| | 73 | ++ | ++ | + | ++ | ++ | 0 | 0 | 0 |
| | 74 | ++ | - | - | + | - | 0 | 0 | 0 |
| | 75 | + | + | - | + | - | 0 | 0 | 0 |
| 55 | 76 | - | - | - | ++ | - | 0 | 0 | 0 |
| | 77 | + | - | - | - | - | 0 | 0 | 0 |
| | 78 | ++ | - | - | - | - | - | - | - |

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TABLE 7 (continued)

| | COMPOUND EX NO. | POWD MDEW | RICE BLAS | LEAF RUST | GRAY MOLD | DOWN MDEW | LEAF SPOT | APPL SCAB | LEAF BLOT |
|----|--------------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| 5 | 79 | - | - | + | - | - | - | - | - |
| | 80 | - | - | + | - | - | 0 | 0 | 0 |
| | 81 | ++ | - | + | - | - | - | - | - |
| | 82 | - | - | - | - | - | 0 | 0 | 0 |
| | 83 | + | - | - | - | + | 0 | 0 | 0 |
| 10 | 84 | + | - | - | - | - | 0 | 0 | 0 |
| | 85 | - | - | - | - | - | 0 | 0 | 0 |
| | 86 | - | - | + | - | - | 0 | 0 | 0 |
| | 87 | - | 0 | - | - | - | 0 | 0 | 0 |
| 15 | 88 | ++ | + | - | ++ | + | 0 | 0 | 0 |
| | 89 | + | + | - | - | + | 0 | 0 | 0 |
| | 90 | ++ | - | - | ++ | - | 0 | 0 | 0 |
| | 91 | +++ | - | - | - | - | 0 | 0 | 0 |
| | 92 | - | - | - | ++ | - | 0 | 0 | 0 |
| 20 | 93 | - | - | - | - | - | 0 | 0 | 0 |
| | 94 | + | + | - | ++ | + | 0 | 0 | 0 |
| | 95 | - | - | - | + | - | 0 | 0 | 0 |
| | 96 | - | + | - | + | + | 0 | 0 | 0 |
| 25 | 97 | - | - | - | - | - | 0 | 0 | 0 |
| | 98 | + | - | - | - | - | 0 | 0 | 0 |
| | 99 | - | - | - | - | - | 0 | 0 | 0 |
| | 100 | + | - | - | - | - | 0 | 0 | 0 |
| | 101 | - | - | - | - | - | 0 | 0 | 0 |
| 30 | 102 | - | - | - | - | - | 0 | 0 | 0 |
| | 103 | + | - | - | - | - | 0 | 0 | 0 |
| | 104 | - | - | - | - | - | 0 | 0 | 0 |
| | 105 | - | - | - | - | + | 0 | 0 | 0 |
| 35 | 106 | ++ | - | - | ++ | - | 0 | 0 | 0 |
| | 107 | + | - | - | - | - | 0 | 0 | 0 |
| | 108 | + | + | + | - | - | 0 | 0 | 0 |
| | 109 | - | - | - | - | - | 0 | 0 | 0 |
| | 110 | +++ | - | + | - | - | 0 | 0 | 0 |
| 40 | 111 | + | - | + | - | + | 0 | 0 | 0 |
| | 112 | - | - | - | - | - | 0 | 0 | 0 |
| | 113 | - | - | - | ++ | - | 0 | 0 | 0 |
| | 114 | - | - | - | - | - | 0 | 0 | 0 |
| 45 | 115 | + | + | + | - | + | 0 | 0 | 0 |
| | 116 | +++ | + | - | ++ | ++ | 0 | 0 | 0 |
| | 117 | + | - | - | - | - | 0 | 0 | 0 |
| | 118 | - | - | - | - | - | 0 | 0 | 0 |
| | 119 | + | - | - | - | - | 0 | 0 | 0 |
| 50 | 120 | + | - | + | ++ | - | 0 | 0 | 0 |
| | 121 | - | - | - | ++ | - | 0 | 0 | 0 |
| | 122 | - | - | - | + | - | 0 | 0 | 0 |
| | 123 | + | + | - | + | - | 0 | 0 | 0 |
| | 124 | + | + | - | ++ | - | 0 | 0 | 0 |
| 55 | 125 | - | - | - | + | - | 0 | 0 | 0 |
| | 126 | ++ | - | - | - | - | 0 | 0 | 0 |
| | 127 | - | - | - | - | - | 0 | 0 | 0 |

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TABLE 7 (continued)

| | COMPOUND EX NO. | POWD MDEW | RICE BLAS | LEAF RUST | GRAY MOLD | DOWN MDEW | LEAF SPOT | APPL SCAB | LEAF BLOT |
|----|--------------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| 5 | 128 | - | + | - | ++ | ++ | 0 | 0 | 0 |
| | 129 | ++ | - | - | - | + | 0 | 0 | 0 |
| | 130 | - | - | - | + | - | 0 | 0 | 0 |
| | 131 | + | - | - | + | - | 0 | 0 | 0 |
| | 132 | ++ | + | + | + | ++ | 0 | 0 | 0 |
| 10 | 133 | - | - | - | - | + | 0 | 0 | 0 |
| | 134 | - | - | - | - | - | 0 | 0 | 0 |
| | 135 | + | - | - | - | - | 0 | 0 | 0 |
| | 136 | + | - | - | - | - | 0 | 0 | 0 |
| 15 | 137 | ++ | + | + | + | - | 0 | 0 | 0 |
| | 138 | ++ | ++ | + | - | + | 0 | 0 | 0 |
| | 139 | ++ | - | + | + | ++ | 0 | 0 | 0 |
| | 140 | +++ | ++ | - | +++ | - | 0 | 0 | 0 |
| | 141 | + | ++ | + | - | ++ | 0 | 0 | 0 |
| 20 | 142 | - | - | - | - | - | 0 | 0 | 0 |
| | 143 | - | - | - | - | - | 0 | 0 | 0 |
| | 144 | + | - | - | - | - | 0 | 0 | 0 |
| | 145 | - | - | - | - | - | 0 | 0 | 0 |
| 25 | 146 | - | - | - | - | - | 0 | 0 | 0 |
| | 147 | - | - | + | 0 | - | 0 | 0 | 0 |

Additional Plant Pathology Tests

30 [0070] Selected compounds were further tested in the greenhouse against various pathogens. The compounds were formulated and applied as foliar sprays as in Test 1. Results are reported in the following Tables 8-10 using the rating scale of Table 7.

[0071] The following abbreviations are used in the Tables:

35 PMW = Wheat Powdery Mildew
PMB = Barley Powdery Mildew
PMG = Grape Powdery Mildew
PMC = Cucumber Powdery Mildew
PMA = Apple Powdery Mildew
40 BG = Grape Botrytis
BT = Tomato Botrytis
BB = Bean Botrytis
DMG = Grape Downy Mildew
LRW = Wheat Leaf Rust
45 LS = Wheat Leaf Spot
LB = Wheat Leaf Blot
AS = Apple Scab
TB = Tomato Blight
PCH = Pseudocercospora herpoturoides

TABLE 8

| COMPOUND EX NO. | PMW | PMB | PMG | PMC | PMA |
|-----------------|-----|-----|-----|-----|-----|
| 1 | 0 | 0 | 0 | 0 | +++ |
| 2 | +++ | ++ | +++ | +++ | +++ |
| 4 | +++ | 0 | 0 | 0 | 0 |
| 6 | ++ | 0 | 0 | 0 | 0 |

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TABLE 8 (continued)

| COMPOUND EX NO. | PMW | PMB | PMG | PMC | PMA |
|-----------------|-----|-----|-----|-----|-----|
| 8 | +++ | 0 | 0 | 0 | 0 |
| 9 | +++ | 0 | 0 | 0 | 0 |
| 11 | - | 0 | 0 | 0 | 0 |
| 12 | +++ | 0 | 0 | 0 | ++ |
| 13 | ++ | 0 | 0 | 0 | 0 |
| 14 | +++ | 0 | 0 | 0 | 0 |
| 16 | +++ | 0 | 0 | 0 | 0 |
| 17 | +++ | 0 | 0 | 0 | 0 |
| 20 | +++ | 0 | 0 | 0 | 0 |
| 23 | +++ | +++ | 0 | ++ | +++ |
| 30 | ++ | 0 | 0 | 0 | 0 |
| 31 | +++ | 0 | 0 | 0 | 0 |
| 38 | +++ | 0 | 0 | 0 | 0 |
| 44 | +++ | 0 | 0 | 0 | ++ |
| 43 | +++ | + | 0 | + | ++ |
| 48 | +++ | 0 | 0 | 0 | 0 |
| 58 | +++ | 0 | 0 | 0 | 0 |
| 61 | +++ | 0 | 0 | 0 | 0 |
| 62 | +++ | 0 | 0 | 0 | 0 |
| 91 | ++ | 0 | 0 | 0 | 0 |
| 98 | - | 0 | 0 | 0 | 0 |
| 109 | +++ | 0 | 0 | 0 | 0 |
| 140 | + | 0 | 0 | 0 | 0 |

TABLE 9

| COMPOUND EX NO. | BG | BT | BB | DMG | LRW |
|-----------------|-----|-----|----|-----|-----|
| 2 | 0 | 0 | 0 | + | + |
| 23 | 0 | 0 | 0 | 0 | + |
| 26 | +++ | ++ | + | ++ | 0 |
| 27 | 0 | - | 0 | 0 | 0 |
| 28 | - | +++ | 0 | 0 | 0 |
| 29 | 0 | ++ | 0 | 0 | 0 |
| 30 | +++ | +++ | 0 | 0 | 0 |
| 44 | 0 | 0 | 0 | 0 | - |
| 46 | 0 | 0 | 0 | 0 | - |
| 60 | 0 | 0 | 0 | ++ | 0 |
| 67 | 0 | +++ | 0 | 0 | 0 |
| 94 | 0 | + | 0 | 0 | 0 |
| 99 | 0 | - | 0 | 0 | 0 |
| 106 | 0 | + | 0 | 0 | 0 |
| 120 | ++ | 0 | 0 | 0 | 0 |
| 121 | ++ | + | 0 | 0 | 0 |
| 140 | 0 | ++ | 0 | 0 | 0 |

TABLE 10

| COMPOUND EX NO. | LS | LB | AS | TB | PCH |
|-----------------|----|----|-----|----|-----|
| 2 | 0 | + | 0 | 0 | 0 |
| 6 | + | 0 | 0 | 0 | 0 |
| 23 | 0 | 0 | 0 | 0 | + |
| 30 | + | 0 | +++ | + | 0 |

Combinations

[0072] Fungal disease pathogens are known to develop resistance to fungicides. When strains resistant to a fungicide do develop, it becomes necessary to apply larger and larger amounts of the fungicide to obtain desired results. To retard the development of resistance to new fungicides, it is desirable to apply the new fungicides in combination with other fungicides. Use of a combination product also permits the product's spectrum of activity to be adjusted.

[0073] Accordingly, another aspect of the invention is a fungicidal combination comprising at least 1% by weight of a compound of formula (1) in combination with a second fungicide.

[0074] Contemplated classes of fungicides from which the second fungicide may be selected include:

- 1) N-substituted azoles, for example propiconazole, triademefon, flusilazol, diniconazole, ethyltrianol, myclobutanil, and prochloraz;
 - 2) pyrimidines, such as fenarimol and nuarimol;
 - 3) morpholines, such as fenpropimorph and tridemorph;
 - 4) piperazines, such as triforine; and
 - 5) pyridines, such as pyrifenoxy.
- Fungicides in these five classes all function by inhibiting sterol biosynthesis. Additional classes of contemplated fungicides, which have other mechanisms of action, include:
- 6) dithiocarbamates, such as maneb and mancozeb;
 - 7) phthalimides, such as captafol;
 - 8) isophthalonitriles, such as chlorothalonil;
 - 9) dicarboximides, such as iprodione;
 - 10) benzimidazoles, such as benomyl and carbendazim;
 - 11) 2-aminopyrimidines, such as ethirimol;
 - 12) carboxamides, such as carboxin; and
 - 13) dinitrophenols, such as dinocap.

[0075] The fungicide combinations of the invention contain at least 1%, ordinarily 20 to 80%, and more typically 50 to 75% by weight of a compound of formula (1).

[0076] Certain combinations within the invention have been found to provide synergistic activity against a number of fungal pathogens. Synergism against powdery mildew and rust has been observed not only in greenhouse tests, but also under field conditions.

[0077] More specifically, synergism has been observed for certain combinations in which the second fungicide component was nuarimol, benomyl, chlorothalonil, prochloraz, propiconazole, triademefon, or tridemorph. The compounds of Examples 2, 12, 23, 30, and 46 were tested in such combinations. In general, it is believed that synergism can be expected under appropriate conditions from combinations comprising a compound of the formula (1) in combination with a sterol inhibiting fungicide of the type that inhibits C-14 demethylation; but, as evidenced by the foregoing list, synergism has also been observed with other classes of fungicides.

[0078] When it is stated that a composition displays synergism, we mean that the percent control of disease observed in a test of the composition exceeds the value predicted by the equation

$$E = X + Y - \frac{XY}{100}$$

where X is the percent control observed in a test of component A applied at rate p, Y is the percent control observed in a test of component B applied at rate q, and E is the expected percent control for the combination of A + B applied at rate p + q. This test is based on an article by S. R. Colby, "Calculating Synergistic and Antagonistic Responses of Herbicide Combinations" Weeds, vol. 15, 20-22 (1967). The test operates on the theory that if components A and B

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each independently kill 50% of disease organisms, then, if used together, after A kills 50% of disease organisms, the best B can be expected to do is kill 50% of the remaining organisms, for an expected total of 75% control.

[0079] A given fungicidal composition may display synergism under certain conditions and not under others. Factors significant in determining whether synergism is displayed include, for example, the application rate, the timing of the application, and the genetic resistance of disease organisms to a component of the composition. When a combination is applied at a rate such that the applied amount of one component alone would afford nearly complete control of the organism, there is little room for improvement, and the synergistic potential of the combination may not be apparent. In regard to timing, if an application of fungicide is made before the fungal disease organism is well established, the organism is more susceptible, and there is less opportunity to show synergistic potential than in the case where the disease organism is well established. On the other hand, if a disease organism is genetically resistant to one component of a combination, so that the applied amount of the one component alone would afford little control of that particular organism, there is more opportunity for the combination to show synergism against that organism than in a case where a similar application rate is used against a non-resistant disease organism.

MITE/INSECT SCREEN

[0080] The compounds of Examples 1-147 were tested for miticidal and insecticidal activity in the following mite/insect screen.

[0081] Each test compound was formulated by dissolving the compound in acetone/alcohol (50:50) mixture containing 23 g of "Toximul R" (sulfonate/nonionic surfactant blend) and 13 g of "Toximul S" (sulfonate/nonionic surfactant blend) per liter. These mixtures were then diluted with water to give the indicated concentrations.

[0082] Twospotted spider mites (*Tetranychus urticae* Koch) and melon aphids (*Aphis gossypii* Glover) were introduced on squash cotyledons and allowed to establish on both leaf surfaces. Other plants in the same treatment pot were left uninfested. The leaves were then sprayed with 5 ml of test solution using a DeVilbiss atomizing sprayer at 10 psi. Both surfaces of the leaves were covered until runoff, and then allowed to dry for one hour. Two uninfested leaves were then excised and placed into a Petri dish containing southern armyworm (*Spodopetra eridania* Cramer).

[0083] Activity on Southern corn rootworm (*Diabrotica undecimpunctata howardi* Barber) was evaluated by adding two ml of tap water, a presoaked corn seed, and 15 g of dry sandy soil to a one ounce plastic container. The soil was treated with 1 mL of test solution containing a predetermined concentration of test compound. After six to 12 hours of drying, five 2-3 instar corn rootworm larvae were added to the individual cups, which were then capped and held at 23°C.

[0084] After standard exposure periods, percent mortality and phytotoxicity were evaluated. Results for the compounds found to be active are reported in Table 11. The remaining compounds showed no activity. The following abbreviations are used in Table 11:

CRW refers to corn rootworm
SAW refers to Southern armyworm
SM refers to twospotted spider mites
MA refers to melon aphids.

Table 11

| EXAMPLE NUMBER | CRW RATE PPM | CRW RESULTS % | SAW SM & MA RATE PPM | SAW RESULTS % | SM RESULTS % | MA RESULTS % |
|----------------|--------------|---------------|----------------------|---------------|--------------|--------------|
| 2 | 12.00 | 0 | 200 | 0 | 0 | 10 |
| 11 | 24.00 | 0 | 400 | 0 | 90 | 0 |
| | 12.00 | 0 | 200 | 0 | 40 | 0 |
| 17 | 24.00 | 0 | 400 | 0 | 40 | 50 |
| 63 | 24.00 | 100 | 400 | 0 | 0 | 0 |
| | 12.00 | 0 | 200 | 0 | 0 | 0 |
| 74 | 24.00 | 100 | 400 | 0 | 0 | 0 |
| | 12.00 | 0 | 200 | 0 | 0 | 0 |
| 97 | 24.00 | 100 | 400 | 0 | 90 | 90 |
| | 12.00 | 100 | 200 | 0 | 0 | 0 |
| 114 | 24.00 | 0 | 400 | 80 | 0 | 0 |
| | 12.00 | 0 | 200 | 0 | 0 | 0 |

Table 11 (continued)

| EXAMPLE NUMBER | CRW RATE PPM | CRW RESULTS % | SAW SM & MA RATE PPM | SAW RESULTS % | SM RESULTS % | MA RESULTS % |
|-------------------|-----------------|------------------|----------------------------|------------------|-----------------|-----------------|
| 131 | 24.00 | 80 | 400 | 0 | 0 | 0 |
| | 12.00 | 0 | 200 | 0 | 0 | 0 |
| 141 | 24.00 | 100 | 400 | 0 | 0 | 0 |
| | 12.00 | 0 | 200 | 0 | 0 | 80 |

Compositions

[0085] The compounds of this invention are applied in the form of compositions which are important embodiments of the invention, and which comprise a compound of this invention and a phytologically-acceptable inert carrier. The compositions are either concentrated formulations which are dispersed in water for application, or are dust or granular formulations which are applied without further treatment. The compositions are prepared according to procedures and formulae which are conventional in the agricultural chemical art, but which are novel and important because of the presence therein of the compounds of this invention. Some description of the formulation of the compositions will be given, however, to assure that agricultural chemists can readily prepare any desired composition.

[0086] The dispersions in which the compounds are applied are most often aqueous suspensions or emulsions prepared from concentrated formulations of the compounds. Such water-soluble, water-suspendable or emulsifiable formulations are either solids usually known as wettable powders, or liquids usually known as emulsifiable concentrates or aqueous suspensions. Wettable powders, which may be compacted to form water dispersible granules, comprise an intimate mixture of the active compound, an inert carrier and surfactants. The concentration of the active compound is usually from about 10% to about 90% by weight. The inert carrier is usually chosen from among the attapulgite clays, the montmorillonite clays, the diatomaceous earths, or the purified silicates. Effective surfactants, comprising from about 0.5% to about 10% of the wettable powder, are found among the sulfonated lignins, the condensed naphthalenesulfonates, the naphthalenesulfonates, the alkylbenzenesulfonates, the alkyl sulfates, and nonionic surfactants such as ethylene oxide adducts of alkyl phenols.

[0087] Emulsifiable concentrates of the compounds comprise a convenient concentration of a compound, such as from about 10% to about 50% by weight of liquid, dissolved in an inert carrier which is either a water miscible solvent or a mixture of water-immiscible organic solvent and emulsifiers. Useful organic solvents include aromatics, especially the xylenes, and the petroleum fractions, especially the high-boiling naphthalenic and olefinic portions of petroleum such as heavy aromatic naphtha. Other organic solvents may also be used, such as the terpenic solvents including rosin derivatives, aliphatic ketones such as cyclohexanone, and complex alcohols such as 2-ethoxyethanol. Suitable emulsifiers for emulsifiable concentrates are chosen from conventional nonionic surfactants such as those mentioned above.

[0088] Aqueous suspensions comprise suspensions of water-insoluble compounds of this invention, dispersed in an aqueous vehicle at a concentration in the range from about 5% to about 50% by weight. Suspensions are prepared by finely grinding the compound, and vigorously mixing it into a vehicle comprised of water and surfactants chosen from the same types discussed above. Inert ingredients, such as inorganic salts and synthetic or natural gums, may also be added, to increase the density and viscosity of the aqueous vehicle. It is often most effective to grind and mix the compound at the same time by preparing the aqueous mixture, and homogenizing it in an implement such as a sand mill, ball mill, or piston-type homogenizer.

[0089] The compounds may also be applied as granular compositions, which are particularly useful for applications to the soil. Granular compositions usually contain from about 0.5% to about 10% by weight of the compound, dispersed in an inert carrier which consists entirely or in large part of clay or a similar inexpensive substance. Such compositions are usually prepared by dissolving the compound in a suitable solvent, and applying it to a granular carrier which has been pre-formed to the appropriate particle size, in the range of from about 0.5 to 3 mm. Such compositions may also be formulated by making a dough or paste of the carrier and compound, and crushing and drying to obtain the desired granular particle size.

[0090] Dusts containing the compounds are prepared simply by intimately mixing the compound in powdered form with a suitable dusty agricultural carrier, such as kaolin clay, ground volcanic rock and the like. Dusts can suitably contain from about 1% to about 10% of the compound.

[0091] The following formulations of compounds of the invention have been prepared, and are typical of compositions useful in the practice of the present invention.

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| A. Emulsifiable Concentrate | |
|--|--------|
| 7-chloro-4-(4-fluorophenoxy)quinoline | 12.50% |
| "TOXIMUL D" (nonionic/anionic surfactant blend) | 1.75% |
| "TOXIMUL H" (nonionic/anionic surfactant blend) | 3.25% |
| "PANASOL AN3N" (naphthalenic solvent) | 64.50% |
| "DOWANOL PM" (propyleneglycol monomethyl ether) | 18.00% |

| B. Dry Flowable | |
|---|--------|
| 7-chloro-4-(4-fluorophenoxy)quinoline | 18.13% |
| "STEPANOL M.E." (anionic surfactant) | 2.50% |
| gum arabic | 0.50% |
| "SELLOGEN HR" (anionic dispersant and wetting agent) | 3.00% |
| "HISIL 233" (silica carrier) | 3.00% |
| "POLYFON H" (lignosulfonate dispersing agent) | 4.00% |
| Barden clay | 8.87% |

| C. Wettable Powder | |
|---------------------------------------|---------|
| 7-chloro-4-(4-fluorophenoxy)quinoline | 78.125% |
| "STEPANOL ME" | 5.000% |
| "HISIL 233" | 5.000% |
| "POLYFON H" | 5.000% |
| Barden clay | 6.875% |

| D. Aqueous Suspension | |
|---|-------|
| 7-chloro-4-(4-fluorophenoxy)quinoline | 12.5% |
| "MAKON 10" (10 moles of ethyleneoxide nonyl phenol surfactant) | 1.0% |
| "ZEOSYL 200" (silica) | 1.0% |
| "POLYFON H" | 0.2% |
| "AF-100" (silicon based antifoam agent) | 0.2% |
| 2% xanthan gum solution | 10.0% |
| tap water | 75.1% |

| E. Aqueous Suspension | |
|---|-------|
| 5,7-dichloro-4-(4-fluorophenoxy)quinoline | 12.5% |
| "MAKON 10" | 1.0% |
| "ZEOSYL 200" | 1.0% |
| "AF-100" | 0.2% |

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(continued)

| E. Aqueous Suspension | |
|-------------------------|-------|
| "POLYFON H" | 0.2% |
| 2% xanthan gum solution | 10.0% |
| tap water | 75.1% |

| F. Aqueous Suspension | |
|---|-------|
| 5,7-dichloro-4-(4-fluorophenoxy)quinoline | 12.5% |
| "TOXIMUL D" | 2.0% |
| "TOXIMUL H" | 2.0% |
| "EXXON 200" (naphthalenic solvent) | 83.5% |

| G. Emulsifiable Concentrate | |
|---------------------------------------|-------|
| 8-chloro-4-(2-chlorophenoxy)quinoline | 17.8% |
| "TOXIMUL D" | 2.5% |
| "TOXIMUL H" | 2.5% |
| "EXXON 200" | 77.2% |

| H. Emulsifiable Concentrate | |
|---------------------------------------|-------|
| 8-chloro-4-(2-chlorophenoxy)quinoline | 12.5% |
| "TOXIMUL D" | 2.5% |
| "TOXIMUL H" | 2.5% |
| "EXXON 200" | 82.5% |

| I. Emulsifiable Concentrate | |
|--|-------|
| 8-chloro-4-(2-chloro-4-fluorophenoxy)quinoline | 17.6% |
| "TOXIMUL D" | 2.5% |
| "TOXIMUL H" | 2.5% |
| "EXXON 200" | 77.4% |

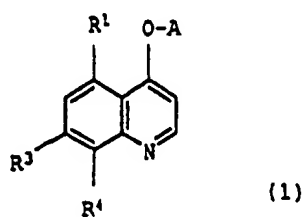
| J. Emulsifiable Concentrate | |
|--|-------|
| 8-chloro-4-(2-chloro-4-fluorophenoxy)quinoline | 12.5% |
| "TOXIMUL D" | 2.5% |
| "TOXIMUL H" | 2.5% |
| "EXXON 200" | 82.5% |

| K. Emulsifiable Concentrate | |
|---|-------|
| 5,7-dichloro-4-(4-fluorophenoxy)quinoline | 12.5% |
| "TOXIMUL D" | 2.0% |
| "TOXIMUL H" | 2.0% |
| "EXXON 200" | 83.5% |

| L. Wettable Powder | |
|--|-------|
| 8-chloro-4-(2-chloro-4-fluorophenoxy)quinoline | 25.8% |
| "SELLOGEN HR" | 5.0% |
| "POLYFON H" | 4.0% |
| "STEPANOL ME DRY" | 2.0% |
| "HISIL 233" | 3.0% |
| Barden clay | 60.2% |

Claims

1. A fungicidal method which comprises applying to the locus of the fungus a fungicidally effective amount of a compound of the formula (1)



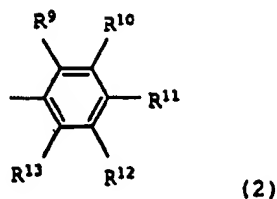
wherein

R¹ to R⁴ are one of the following:-

- a) R³ is Cl and R¹ and R⁴ are H;
- b) R³ is Br and R¹ and R⁴ are H;
- c) R¹ and R³ are Cl and R⁴ is H;
- d) R⁴ is Cl and R¹ and R³ are H;

A is

- a) (C₃-C₈) cycloalkyl or cycloalkenyl;
- b) a phenyl group of the formula (2)



wherein R⁹ to R¹³ are independently

- H,
- CN,
- NO₂,
- OH,
- halo,
- I,
- (C₁-C₄) alkyl,

(C₃-C₄) branched alkyl,
 (C₂-C₄) acyl,
 halo (C₁-C₄) alkyl,
 hydroxy (C₁-C₄) alkyl,
 (C₁-C₄) alkoxy,
 halo (C₁-C₄) alkoxy,
 (C₁-C₄) alkylthio,
 halo (C₁-C₄) alkylthio,

an optionally substituted group phenyl-W-, where W is a bond, O, SiR²⁰R²¹R²² or OSiR²⁰R²¹R²² where R²⁰, R²¹, and R²² are H, a C₁-C₆ alkyl group, straight chain or branched, phenyl or substituted phenyl, provided that at least one of R²⁰, R²¹, and R²² is other than H, or R¹¹ and R¹² or R¹² and R¹³ combine to form a carbocyclic ring, provided that unless all of the R⁹ to R¹³ are H or F, then at least two of R⁹ to R¹³ are H; or an acid addition salt of a compound of formula (1), or an N-oxide of a compound of formula (1);

wherein the term "substituted" as used herein means substituted by up to three groups selected from halo, I, (C₁ to C₁₀) alkyl, branched (C₃-C₆) alkyl, halo (C₁-C₄) alkyl, hydroxy (C₁-C₄) alkyl, C₁-C₄ alkoxy, halo C₁-C₄ alkoxy, phenoxy, phenyl, NO₂, OH, CN (C₁-C₄) alkanoyloxy, or benzyloxy, but not including any such method for the therapeutic treatment of the human or animal body.

2. A compound of formula (1) as defined in Claim 1, provided that the following compounds are excluded:

- 1) compounds wherein R³ is C1, R¹ and R⁴ are H, and A is phenyl, 4-chlorophenyl, or 4-fluorophenyl; and
- 2) 7-chloro-4-[3-(trifluoromethyl)phenoxy]-quinoline;
- 3) 7-chloro-4-(4-chloro-3,5-dimethylphenoxy)-quinoline;
- 4) 7-chloro-4-(4-chloro-3-methylphenoxy)-quinoline; or an acid addition salt or an N-oxide of a compound of formula (1).

3. A compound of claim 2 wherein R¹ is H or Cl, R³ is Cl, and R⁴ is H.

4. The compound of claim 3 which is 5,7-di-chloro-4- (4-fluorophenoxy) quinoline, or the 1-oxide thereof.

5. A compound of claim 2 wherein R¹ and R³ are H and R⁴ is Cl.

6. A compound of claim 5 wherein A is 2-chlorophenyl or 2-chloro-4-fluorophenyl.

7. 7-chloro-4-[2-(trifluoromethyl)phenoxy]quinoline, or the 1-oxide thereof.

8. 5,7-di-chloro-4-phenoxyquinoline, or the 1-oxide thereof.

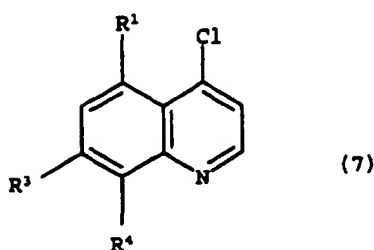
9. 7-chloro-4-(2-nitrophenoxy) quinoline, or the 1-oxide thereof.

10. A fungicidal formulation comprising as active ingredient a compound as claimed in any one of claims 2 to 9.

11. A fungicidal combination comprising a compound as claimed in any one of claims 2 to 10, in combination with a second fungicide.

12. A process for preparing a compound as claimed in claim 2, which comprises

- a) condensing a compound for formula (7)



wherein R¹, R³ and R⁴ are as defined in claim 1 with a compound of formula (8)

HO-A

(8)

wherein A is as defined in claim 1 to provide a compound of formula (1), or

b) oxidizing a compound of formula (1) to provide the corresponding N-oxide.

20 13. A compound of claim 2 which is:

2-[(7-chloro-4-quinolinyloxy)benzonitrile
 7-chloro-4-(3-chlorophenoxy)quinoline
 4-(2-bromophenoxy)-7-chloroquinoline
 7-chloro-4-(2,4-difluorophenoxy)quinoline
 7-chloro-4-(2,3,5,6-tetrafluorophenoxy)quinoline
 7-chloro-4-(2-chlorophenoxy)quinoline
 7-chloro-4-(2,6-difluorophenoxy)quinoline
 7-chloro-4-(2-chloro-4-fluorophenoxy)quinoline, 1-oxide
 7-chloro-4-(4-fluorophenoxy)quinoline, hydrochloride
 7-chloro-4-[2-(i-propyl)phenoxy]quinoline
 7-chloro-4-(pentafluorophenoxy)quinoline
 7-chloro-4-(3-chloro-4-fluorophenoxy)quinoline
 7-chloro-4-(4-phenoxyphenoxy)quinoline
 7-chloro-4-[4-(t-butyl)phenoxy]quinoline
 7-chloro-4-[4-(i-propyl)phenoxy]quinoline
 7-chloro-4-(3-fluorophenoxy)quinoline
 7-chloro-4-(2-fluorophenoxy)quinoline
 7-chloro-4-(4-methylphenoxy)quinoline
 7-chloro-4-(4-methoxyphenoxy)quinoline
 7-chloro-4-(2-methoxyphenoxy)quinoline
 7-chloro-4-(2-methylphenoxy)quinoline
 7-chloro-4-(3-nitrophenoxy)quinoline
 7-chloro-4-(2-nitrophenoxy)quinoline
 7-chloro-4-(4-nitrophenoxy)quinoline
 7-chloro-4-(2-(trifluoromethyl)phenoxy)quinoline
 7-chloro-4-[4-(trifluoromethyl)phenoxy]quinoline
 4-(2-bromo-4-fluorophenoxy)-7-chloroquinoline
 7-chloro-4-(2,6-dibromo-4-fluoro-phenoxy)quinoline
 7-chloro-4-[3-(t-butyl)phenoxy]quinoline
 7-chloro-4-[2-(t-butyl)phenoxy]quinoline
 4-[(7-chloro-4-quinolinyloxy)phenol
 2-[(7-chloro-4-quinolinyloxy)phenol
 4-([1,1'-biphenyl]-2-yloxy)-7-chloroquinoline
 7-chloro-4-(2-chloro-4-fluorophenoxy)quinoline
 7-chloro-4-(2-iodophenoxy)quinoline
 7-chloro-4-[4-(trifluoromethylthio)phenoxy]quinoline

7-chloro-4-(3-methylphenoxy)quinoline
 4-[(7-chloro-4-quinolinyloxy)benzonitrile
 3-[(7-chloro-4-quinolinyloxy)benzonitrile
 4-(4-bromophenoxy)-7-chloroquinoline
 5 7-chloro-4-(4-iodophenoxy)quinoline
 4-(3-bromophenoxy)-7-chloroquinoline
 7-chloro-4-(2-methyl-4-fluorophenoxy)quinoline
 7-chloro-4-(4-fluorophenoxy)-2-methylquinoline
 7-chloro-4-(2,4-dinitrophenoxy)quinoline
 10 4-[(1,1'-biphenyl)-4-yloxy]-7-chloroquinoline
 3-[(7-chloro-4-quinolinyloxy)phenol
 7-chloro-4-(2-phenoxyphenoxy)quinoline
 7-chloro-4-[2-(methylthio)phenoxy]quinoline
 4-(2,4-dibromophenoxy)-7-chloroquinoline
 15 7-chloro-4-(2,6-dimethylphenoxy)quinoline, or
 4-(4-bromo-2-fluorophenoxy)-7-chloroquinoline

14. A compound of Claim 4 which is:

20 5,7-dichloro-4-(4-fluorophenoxy)quinoline, 1-oxide
 5,7-dichloro-4-(4-fluorophenoxy)quinoline
 5,7-dichloro-4-(2,4-difluorophenoxy)quinoline
 5,7-dichloro-4-(2-nitrophenoxy)quinoline
 5,7-dichloro-4-[2-(trifluoromethyl)phenoxy]quinoline
 25 5,7-dichloro-4-(2-fluorophenoxy)quinoline
 5,7-dichloro-4-(2-chlorophenoxy)quinoline
 5,7-dichloro-4-(2-cyanophenoxy)quinoline
 5,7-dichloro-4-(2-chloro-4-fluorophenoxy)quinoline
 5,7-dichloro-4-(3-bromophenoxy)quinoline
 30 5,7-dichloro-4-phenoxyquinoline, or
 4-[(5,7-dichloro-4-quinolinyloxy)benzonitrile

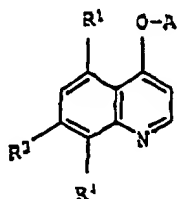
15. A compound of Claim 6 which is:

35 8-chloro-4-(2-chlorophenoxy)quinoline
 8-chloro-4-[2-(trifluoromethyl)phenoxy]quinoline
 4-(2-bromophenoxy)-8-chloroquinoline
 8-chloro-4-(2-fluorophenoxy)quinoline
 8-chloro-4-(2-chloro-4-fluorophenoxy)quinoline
 40 8-chloro-4-(4-(i-propyl)phenoxy)quinoline
 8-chloro-4-(2,4-dichlorophenoxy)quinoline
 8-chloro-4-(2-cyanophenoxy)quinoline
 8-chloro-4-(2-iodophenoxy)quinoline
 8-chloro-4-(2,4-difluorophenoxy)quinoline
 45 8-chloro-4-(3-chlorophenoxy)quinoline
 8-chloro-4-(2-methylphenoxy)quinoline
 8-chloro-4-(2,6-dichlorophenoxy)quinoline
 8-chloro-4-(2-methoxyphenoxy)quinoline
 8-chloro-4-(4-methoxyphenoxy)quinoline
 50 8-chloro-4-(2,4-dichloro-6-fluorophenoxy)quinoline
 8-chloro-4-(2-ethoxyphenoxy)quinoline
 8-chloro-4-(4-fluoro-2-methylphenoxy)quinoline
 8-chloro-4-(4-chloro-2-fluorophenoxy)quinoline
 8-chloro-4-(2,4-dibromophenoxy)quinoline
 55 8-chloro-4-(4-fluoro-2-nitrophenoxy)quinoline
 8-chloro-4-(2,4,6-trichlorophenoxy)quinoline
 8-chloro-4-(2-nitrophenoxy)quinoline
 8-chloro-4-(2,6-dibromo-4-fluorophenoxy)quinoline

8-chloro-4-(3-methylphenoxy)quinoline
 8-chloro-4-(4-ethoxyphenoxy)quinoline
 8-chloro-4-(4-chloro-2-methylphenoxy)quinoline
 4-(4-chloro-3,5-dimethylphenoxy)-8-chloroquinoline
 4-(4-chloro-2-nitrophenoxy)-8-chloroquinoline
 8-chloro-4-(2-ethylphenoxy)quinoline
 8-chloro-4-[2-(methylthio)phenoxy]quinoline
 8-chloro-4-(4-methylphenoxy)quinoline
 8-chloro-4-(2,3-dimethylphenoxy)quinoline
 8-chloro-4-(3,4-dimethylphenoxy)quinoline
 8-chloro-4-[(4-trifluoromethoxy)phenoxy]quinoline
 8-chloro-4-(2,5-dichlorophenoxy)quinoline
 8-chloro-4-(2,6-dimethylphenoxy)quinoline
 8-chloro-4-(3,5-dimethylphenoxy)quinoline
 8-chloro-4-(2-chloro-6-methylphenoxy)quinoline
 8-chloro-4-(2,5-dimethylphenoxy)quinoline
 8-chloro-4-[2-chloro-5-(trifluoromethyl)phenoxy]quinoline
 4-(2-chloro-4-nitrophenoxy)-8-chloroquinoline, or
 8-chloro-4-(4-ethylphenoxy)quinoline.

Patentansprüche

1. Fungizides Verfahren, welches das Aufbringen einer fungizid wirksamen Menge einer Verbindung der Formel (1)



(1)

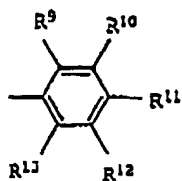
wobei

R¹ bis R⁴ einer der Folgenden sind:

- a) R³ ist Cl und R¹ und R⁴ sind H;
- b) R³ ist Br und R¹ und R⁴ sind H;
- c) R¹ und R³ sind Cl und R⁴ ist H;
- d) R⁴ ist Cl und R¹ und R³ sind H;

A ist:

- a) (C₃-C₉)-Cycloalkyl oder -Cycloalkenyl;
- b) eine Phenylgruppe der Formel (2)



(2)

wobei R⁹ bis R¹³ unabhängig voneinander sind;

H,
CN,
NO₂,
OH,
Halo;

I,
(C₁-C₄)-Alkyl,
verzweigtes (C₃-C₄)-Alkyl,
(C₂-C₄)-Acyloxy,
Halo-(C₁-C₄)-Alkyl,
Hydroxy-(C₁-C₄)-Alkyl,
(C₁-C₄)-Alkoxy,
Halo-(C₁-C₄)-Alkoxy,
(C₁-C₄)-Alkylthio,
Halo-(C₁-C₄)-Alkylthio,

eine gegebenenfalls substituierte Phenyl-W-Gruppe,

wobei W eine Bindung, O, SiR²⁰R²¹R²² oder OSiR²⁰R²¹R²² ist, wobei R²⁰, R²¹ und R²² H, eine geradkettige oder verzweigte (C₁-C₆)-Alkylgruppe, Phenyl oder substituiertes Phenyl sind, mit der Massgabe, dass wenigstens einer der R²⁰, R²¹ und R²² nicht H ist oder sich R¹¹ und R¹² oder R¹² und R¹³ verbinden, um einen carbocyclischen Ring zu bilden, mit der Massgabe, dass, wenn nicht alle der R⁹ bis R¹³ H oder F sind, wenigstens zwei der R⁹ bis R¹³ H sind;

oder eines Säureadditionssalzes einer Verbindung der Formel (1) oder eines N-Oxids einer Verbindung der Formel (1) auf den Ort des Pilzes umfasst,

wobei die Bezeichnung "substituiert", wie hierin verwendet, substituiert mit bis zu drei Gruppen ausgewählt aus Halo, I, (C₁-C₁₀)-Alkyl, verzweigtes (C₃-C₆)-Alkyl, Halo-(C₁-C₄)-Alkyl, Hydroxy-(C₁-C₄)-Alkyl, (C₁-C₄)-Alkoxy, Halo-(C₁-C₄)-Alkoxy, Phenoxy, Phenyl, NO₂, OH, CN-(C₁-C₄)-Alkanoyloxy oder -Benzyloxy bedeutet, wobei irgendein solches Verfahren zur therapeutischen Behandlung des humanen oder tierischen Körpers nicht eingeschlossen ist.

2. Verbindung der Formel (1) nach Anspruch 1 oder ein Säureadditionssalz oder ein N-Oxid einer Verbindung der Formel (1), mit der Massgabe, dass die folgenden Verbindungen ausgeschlossen sind:

- 1) Verbindungen, bei denen R³ Cl ist, R¹ und R⁴ H sind und A Phenyl, 4-Chlorphenyl oder 4-Fluorphenyl ist; und
- 2) 7-Chlor-4-[3-(trifluormethyl)phenoxy]-quinolin;
- 3) 7-Chlor-4-(4-chlor-3,5-dimethylphenoxy)-quinolin;
- 4) 7-Chlor-4-(4-chlor-3-methylphenoxy)-quinolin.

3. Verbindung nach Anspruch 2, wobei R¹ H oder Cl ist, R² H ist, R³ Cl ist und R⁴ H ist.

4. Verbindung nach Anspruch 3, die 5,7-Di-chlor-4-(4-fluorphenoxy)quinolin oder das 1-Oxid davon ist.

5. Verbindung nach Anspruch 2, wobei R¹ bis R³ H sind und R⁴ Cl ist.

6. Verbindung nach Anspruch 5, wobei A 2-Chlorphenyl oder 2-Chlor-4-fluorphenyl ist.

7. 7-Chlor-4-[2-(trifluormethyl)phenoxy]quinolin oder das 1-Oxid davon.

8. 5,7-Di-Chlor-4-phenoxyquinolin oder das 1-Oxid davon.

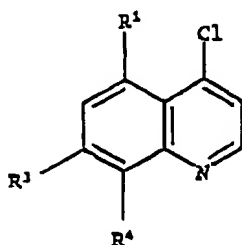
9. 7-Chlor-4-(2-nitrophenoxy)quinolin oder das 1-Oxid davon.

10. Fungizide Formulierung umfassend eine Verbindung nach einem der Ansprüche 2 bis 9 als Wirkstoff.

11. Fungizide Kombination umfassend eine Verbindung nach einem der Ansprüche 2 bis 9 in Verbindung mit einem zweiten Fungizid.

12. Verfahren zur Herstellung einer Verbindung nach Anspruch 2, welches

a) Kondensieren einer Verbindung der Formel (7)



(7)

wobei R¹, R³ und R⁴ wie in Anspruch 1 definiert sind,
mit einer Verbindung der Formel (8)

HO-A

(8)

wobei A wie in Anspruch 1 definiert ist, um eine Verbindung der Formel (1) bereitzustellen, oder
b) Oxidieren einer Verbindung der Formel (1), um das entsprechende N-Oxid bereitzustellen,

umfasst.

13. Verbindung nach Anspruch 2, die

2-[(7-Chlor-4-quinolinyloxy]benzonitril
7-Chlor-4-(3-chlorphenoxy)quinolin
4-(2-Bromphenoxy)-7-chlorquinolin
7-Chlor-4-(2,4-difluorphenoxy)quinolin
7-Chlor-4-(2,3,5,6-tetrafluorphenoxy)quinolin
7-Chlor-4-(2-chlorphenoxy)quinolin
7-Chlor-4-(2,6-difluorphenoxy)quinolin
7-Chlor-4-(2-Chlor-4-fluorphenoxy)quinolin,
1-Oxid
7-Chlor-4-(4-fluorphenoxy)quinoline,
Hydrochlorid
7-Chlor-4-[(2-i-propyl)phenoxy]quinolin
7-Chlor-4-(pentafluorphenoxy)quinolin
7-Chlor-4-(3-chlor-4-fluorphenoxy)quinolin
7-Chlor-4-(4-phenoxyphenoxy)quinolin
7-Chlor-4-[4-(t-butyl)phenoxy]quinolin
7-Chlor-4-[(4-i-propyl)phenoxy]quinolin
7-Chlor-4-(3-fluorphenoxy)quinolin
7-Chlor-4-(2-fluorphenoxy)quinolin
7-Chlor-4-(4-methylphenoxy)quinolin
7-Chlor-4-(4-methoxyphenoxy)quinolin
7-Chlor-4-(2-methoxyphenoxy)quinolin
7-Chlor-4-(2-methylphenoxy)quinolin
7-Chlor-4-(3-nitrophenoxy)quinolin
7-Chlor-4-(2-nitrophenoxy)quinolin
7-Chlor-4-(4-nitrophenoxy)quinolin
7-Chlor-4-[2-(trifluormethyl)phenoxy]quinolin
7-Chlor-4-[4-(trifluormethyl)phenoxy]quinolin
4-(2-Brom-4-fluorphenoxy)-7-chlorquinolin
7-Chlor-4-(2,6-dibrom-4-fluor-phenoxy)quinolin

7-Chlor-4-(3-(t-butyl)phenoxy)quinolin
 7-Chlor-4-(2-(t-butyl)phenoxy)quinolin
 4-[(7-Chlor-4-quinolinyloxy)phenol
 2-[(7-Chlor-4-quinolinyloxy)phenol
 4-[(1,1'-biphenyl)-2-yloxy]-7-chlorquinolin
 7-Chlor-4-(2-chlor-4-fluorophenoxy)quinolin
 7-Chlor-4-(2-iodphenoxy)quinolin
 7-Chlor-4-(4-[(trifluormethyl)thio]phenoxy)quinolin
 7-Chlor-4-(3-methylphenoxy)quinolin
 4-[(7-Chlor-4-quinolinyloxy)benzotrile
 3-[(7-Chlor-4-quinolinyloxy)benzotrile
 4'-(4-Bromphenoxy)-7-chlorquinolin
 7-Chlor-4-(4-iodphenoxy)quinolin
 4-(3-Bromphenoxy)-7-chlorquinolin
 7-Chlor-4-(2-methyl-4-fluorophenoxy)quinolin
 7-Chlor-4-(4-fluorophenoxy)-2-methylquinolin
 7-Chlor-4-(2,4-dinitrophenoxy)quinolin
 4-[(1,1'-biphenyl)-4-yloxy]-7-chlorquinolin
 3-[(7-Chlor-4-quinolinyloxy)phenol
 7-Chlor-4-(2-phenoxyphenoxy)quinolin
 7-Chlor-4-[2-(methylthio)phenoxy]quinolin
 4-(2,4-Dibromphenoxy)-7-chlorquinolin
 7-Chlor-4'-(2,6-dimethylphenoxy)quinolin oder
 4-(4-Brom-2-fluorophenoxy)-7-chlorquinolin

ist.

14. Verbindung nach Anspruch 4, die

5,7-Dichlor-4-(4-fluorophenoxy)quinolin,
 1-Oxid
 5,7-Dichlor-4-(4-fluorophenoxy)quinolin
 5,7-Dichlor-4-(2,4-difluorophenoxy)quinolin
 5,7-Dichlor-4-(2-nitrophenoxy)quinolin
 5,7-Dichlor-4-[2-(trifluormethyl)phenoxy]quinolin
 5,7-Dichlor-4-(2-fluorophenoxy)quinolin
 5,7-Dichlor-4-(2-chlorphenoxy)quinolin
 5,7-Dichlor-4-(2-cyanphenoxy)quinolin
 5,7-Dichlor-4-(2-chlor-4-fluorophenoxy)quinolin
 5,7-Dichlor-4-(3-bromphenoxy)quinolin
 5,7-Dichlor-4-phenoxyquinolin oder
 4-[(5,7-Dichlor-4-quinolinyloxy)benzotrile

ist.

15. Verbindung nach Anspruch 6, die

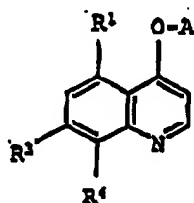
8-Chlor-4-(2-chlorphenoxy)quinolin
 8-Chlor-4-[2-(trifluormethyl)phenoxy]quinolin
 4-(2-Bromphenoxy)-8-chlorquinolin
 8-Chlor-4-(2-fluorophenoxy)quinolin
 8-Chlor-4-(2-chlor-4-fluorophenoxy)quinolin
 8-Chlor-4-[4-(1-propyl)phenoxy]quinolin
 8-Chlor-4-(2,4-dichlorphenoxy)quinolin
 8-Chlor-4-(2-cyanphenoxy)quinolin
 8-Chlor-4-(2-iodphenoxy)quinolin
 8-Chlor-4-(2,4-difluorophenoxy)quinolin
 8-Chlor-4-(3-chlorphenoxy)quinolin

8-Chlor-4-(2-methylphenoxy)quinolin
 8-Chlor-4-(2,6-dichlorphenoxy)quinolin
 8-Chlor-4-(2-methoxyphenoxy)quinolin
 8-Chlor-4-(4-methoxyphenoxy)quinolin
 5 8-Chlor-4-(2,4-dichlor-6-fluorphenoxy)quinolin
 8-Chlor-4-(2-ethoxyphenoxy)quinolin
 8-Chlor-4-(4-fluor-2-methylphenoxy)quinolin
 8-Chlor-4-(4-chlor-2-fluorphenoxy)quinolin
 8-Chlor-4-(2,4-dibromphenoxy)quinolin
 10 8-Chlor-4-(4-fluor-2-nitrophenoxy)quinolin
 8-Chlor-4-(2,4,6-trichlorphenoxy)quinolin
 8-Chlor-4-(2-nitrophenoxy)quinolin
 8-Chlor-4-(2,6-dibrom-4-fluorphenoxy)quinolin
 8-Chlor-4-(3-methylphenoxy)quinolin
 15 8-Chlor-4-(4-ethoxyphenoxy)quinolin
 8-Chlor-4-(4-chlor-2-methylphenoxy)quinolin
 4-(4-Chlor-3,5-dimethylphenoxy)-8-chlorquinolin
 4-(4-Chlor-2-nitrophenoxy)-8-chlorquinolin
 8-Chlor-4-(2-ethylphenoxy)quinolin
 20 8-Chlor-4-[2-(methylthio)phenoxy]quinolin
 8-Chlor-4-(4-methylphenoxy)quinolin
 8-Chlor-4-(2,3-dimethylphenoxy)quinolin
 8-Chlor-4-(3,4-dimethylphenoxy)quinolin
 8-Chlor-4-[4-(trifluormethoxy)phenoxy]quinolin
 25 8-Chlor-4-(2,5-dichlorphenoxy)quinolin
 8-Chlor-4-(2,6-dimethylphanoxy)quinolin
 8-Chlor-4-(3,5-dimethylphenoxy)quinolin
 8-Chlor-4-(2-chlor-6-methylphenoxy)quinolin
 8-Chlor-4-(2,5-dimethylphenoxy)quinolin
 30 8-Chlor-4-[2-chlor-5-(trifluormethyl)phenoxy]quinolin
 4-(2-Chlor-4-nitrophenoxy)-8-chlorquinolin oder
 8-Chlor-4-(4-ethylphenoxy)quinolin

ist.

Revendications

1. Procédé de lutte antifongique, qui consiste à appliquer, en un lieu où peuvent vivre des fungi, une certaine quantité, suffisante pour tuer effectivement les fungi, d'un composé de formule (1) :



(1)

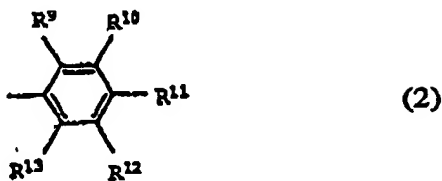
dans laquelle

- les symboles R¹ à R⁴ ont l'une des significations suivantes :

- a) R³ représente un atome de chlore et R¹ et R⁴ représentent des atomes d'hydrogène,
 b) R³ représente un atome de brome et R¹ et R⁴ représentent des atomes d'hydrogène,
 c) R¹ et R³ représentent des atomes de chlore et R⁴ représente un atome d'hydrogène, ou
 d) R⁴ représente un atome de chlore et R¹ et R³ représentent des atomes d'hydrogène,

- et A représente

- a) un groupe cycloalkyle ou cycloalcényle en C₃₋₈, ou
b) un groupe phényle de formule (2) :



dans laquelle les symboles R⁹ à R¹³ représentent chacun, indépendamment :

- un atome d'hydrogène,
- un groupe cyano,
- un groupe nitro,
- un groupe hydroxyle,
- un atome d'halogène,
- un atome d'iode,
- un groupe allyle en C₁₋₄,
- un groupe alkyle ramifié en C₃₋₄,
- un groupe acyle en C₂₋₄,
- un groupe halogénoalkyle en C₁₋₄,
- un groupe hydroxyalkyle en C₁₋₄,
- un groupe alcoxy en C₁₋₄,
- un groupe halogénoalcoxy en C₁₋₄,
- un groupe alkylthio en C₁₋₄,
- un groupe halogénoalkylthio en C₁₋₄,
- un groupe phényl-W-, éventuellement substitué,
où W représente une liaison ou un atome d'oxygène,
- un groupe de formule -SiR²⁰R²¹R²² ou -O-SiR²⁰R²¹R²²,
où R²⁰, R²¹ et R²² représentant chacun un atome d'hydrogène, un groupe alkyle en C₁₋₆ à chaîne droite ou ramifiée, ou un groupe phényle, substitué ou non,
sous réserve qu'au moins l'un des symboles R²⁰, R²¹ et R²² représente autre chose qu'un atome d'hydrogène,

ou bien les symboles R¹¹ et R¹², ou R¹² et R¹³, représentent ensemble un carbocycle,
sous réserve que, excepté le cas où tous les symboles R⁹ à R¹³ représentent des atomes d'hydrogène ou de fluor, au moins deux de ces symboles R⁹ à R¹³ représentent des atomes d'hydrogène,

ou d'un sel d'addition d'acide d'un composé de formule (1), ou encore d'un N-oxyde d'un composé de formule (1) ;
le terme "substitué" étant utilisé ici pour qualifier un groupe portant jusqu'à trois substituants choisis parmi halogéno-, iodo-, alkyle en C₁₋₁₀, alkyle ramifié en C₃₋₆, halogénoalkyle en C₁₋₄, hydroxyalkyle en C₁₋₄, alcoxy en C₁₋₄, halogénoalcoxy en C₁₋₄, phénoxy, phényle, nitro, hydroxy, cyano, alcanoyloxy en C₁₋₄ et benzyloxy ;
mais à l'exclusion de tout procédé de ce type servant à un traitement thérapeutique chez l'homme ou chez l'animal.

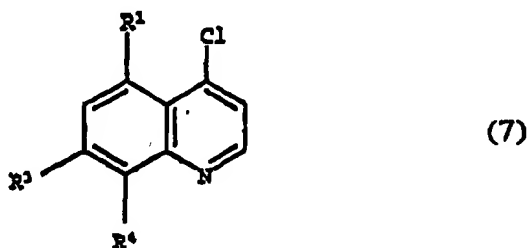
2. Composé de formule (1) définie dans la revendication 1, ou sel d'addition d'acide ou N-oxyde d'un tel composé, à l'exclusion des composés suivants :

- 1) les composés dans lesquels R³ représente un atome de chlore, R¹ et R⁴ représentent des atomes d'hydrogène, et A représente un groupe phényle, 4-chlorophényle ou 4-fluorophényle ;
- 2) la 7-chloro-4-(3-trifluorométhylphénoxy)quinoléine ;
- 3) la 7-chloro-4-(4-chloro-3,5-diméthylphénoxy)quinoléine ; et
- 4) la 7-chloro-4-(4-chloro-3-méthylphénoxy)quinoléine.

3. Composé conforme à la revendication 2, dans lequel R¹ représente un atome d'hydrogène ou de chlore, R² re-

présente un atome d'hydrogène, R³ représente un atome de chlore, et R⁴ représente un atome d'hydrogène.

4. Composé conforme à la revendication 3, qui est la 5,7-dichloro-4-(4-fluorophénoxy)quinoléine, ou son 1-oxyde.
5. Composé conforme à la revendication 2, dans lequel les symboles R¹ à R³ représentent des atomes d'hydrogène et R⁴ représente un atome de chlore.
6. Composé conforme à la revendication 5, dans lequel A représente un groupe 2-chlorophényle ou 2-chloro-4-fluorophényle.
7. 7-Chloro-4-(2-trifluorométhylphénoxy)quinoléine, ou son 1-oxyde.
8. 5,7-Dichloro-4-phénoxyquinoléine, ou son 1-oxyde.
9. 7-Chloro-4-(2-nitrophénoxy)quinoléine, ou son 1-oxyde.
10. Formulation fongicide comportant, en qualité d'ingrédient actif, un composé conforme à l'une des revendications 2 à 9.
11. Composition fongicide comportant un composé conforme à l'une des revendications 2 à 9, combiné avec un deuxième fongicide.
12. Procédé de préparation d'un composé conforme à la revendication 2, qui comporte
 - a) le fait de condenser un composé de formule (7)



dans laquelle R¹, R³ et R⁴ ont les significations indiquées dans la revendication 1, avec un composé de formule (8) :



dans laquelle A a la signification indiquée dans la revendication 1, ou bien

b) le fait d'oxyder un composé de formule (1) pour obtenir le N-oxyde correspondant.

13. Composé conforme à la revendication 2, qui est :

le 2-((7-chloro-4-quinolyl)oxy)benzonitrile,
 la 7-chloro-4-(3-chlorophénoxy)quinoléine,
 la 4-(2-bromophénoxy)-7-chloroquinoléine,
 la 7-chloro-4-(2,4-difluorophénoxy)quinoléine,
 la 7-chloro-4-(2,3,5,6-tétrafluorophénoxy)quinoléine,
 la 7-chloro-4-(2-chlorophénoxy)quinoléine,
 la 7-chloro-4-(2,6-difluorophénoxy)quinoléine,
 le 7-chloro-4-(2-chloro-4-fluorophénoxy)quinoléine-1-oxyde,
 le chlorhydrate de 7-chloro-4-(4-fluorophénoxy)quinoléine,

la 7-chloro-4-(2-isopropylphénoxy)quinoléine,
 la 7-chloro-4-(pentafluorophénoxy)quinoléine,
 la 7-chloro-4-(3-chloro-4-fluorophénoxy)quinoléine,
 la 7-chloro-4-(4-phénoxyphénoxy)quinoléine,
 5 la 7-chloro-4-(4-tertobutylphénoxy)quinoléine,
 la 7-chloro-4-(4-isopropylphénoxy)quinoléine,
 la 7-chloro-4-(3-fluorophénoxy)quinoléine,
 la 7-chloro-4-(2-fluorophénoxy)quinoléine,
 la 7-chloro-4-(4-méthylphénoxy)quinoléine,
 10 la 7-chloro-4-(4-méthoxyphénoxy)quinoléine,
 la 7-chloro-4-(2-méthoxyphénoxy)quinoléine,
 la 7-chloro-4-(2-méthylphénoxy)quinoléine,
 la 7-chloro-4-(3-nitrophénoxy)quinoléine,
 la 7-chloro-4-(2-nitrophénoxy)quinoléine,
 15 la 7-chloro-4-(4-nitrophénoxy)quinoléine,
 la 7-chloro-4-[2-(trifluorométhyl)phénoxy]quinoléine,
 la 7-chloro-4-[4-(trifluorométhyl)phénoxy]quinoléine,
 la 4-(2-bromo-4-fluorophénoxy)-7-chloroquinoléine,
 la 7-chloro-4-(2,6-dibromo-4-fluorophénoxy)quinoléine,
 20 la 7-chloro-4-(3-tertobutylphénoxy)quinoléine,
 la 7-chloro-4-(2-tertobutylphénoxy)quinoléine,
 le 4-[(7-chloro-4-quinolyl)oxy]phénol,
 le 2-[(7-chloro-4-quinolyl)oxy]phénol,
 la 4-[(1,1'-biphényl)-2-yloxy]-7-chloroquinoléine,
 25 la 7-chloro-4-(2-chloro-4-fluorophénoxy)quinoléine,
 la 7-chloro-4-(2-iodophénoxy)quinoléine,
 la 7-chloro-4-[4-(trifluorométhylthio)phénoxy]quinoléine,
 la 7-chloro-4-(3-méthylphénoxy)quinoléine,
 le 4-[(7-chloro-4-quinolyl)oxy]benzonitrile,
 30 le 3-[(7-chloro-4-quinolyl)oxy]benzonitrile,
 la 4-(4-bromophénoxy)-7-chloroquinoléine,
 la 7-chloro-4-(4-iodophénoxy)quinoléine,
 la 4-(3-bromophénoxy)-7-chloroquinoléine,
 la 7-chloro-4-(2-méthyl-4-fluorophénoxy)quinoléine,
 35 la 7-chloro-4-(4-fluorophénoxy)-2-méthylquinoléine,
 la 7-chloro-4-(2,4-dinitrophénoxy)quinoléine,
 la 4-[(1,1'-biphényl)-4-yloxy]-7-chloroquinoléine,
 le 3-[(7-chloro-4-quinolyl)oxy]phénol,
 la 7-chloro-4-(2-phénoxyphénoxy)quinoléine,
 40 la 7-chloro-4-[2-(méthylthio)phénoxy]quinoléine,
 la 4-(2,4-dibromophénoxy)-7-chloroquinoléine,
 la 7-chloro-4-(2,6-diméthylphénoxy)quinoléine, ou
 la 4-(4-bromo-2-fluorophénoxy)-7-chloroquinoléine.

45 14. Composé conforme à la revendication 4, qui est :

le 5,7-dichloro-4-(4-fluorophénoxy)quinoléine-1-oxyde,
 la 5,7-dichloro-4-(4-fluorophénoxy)quinoléine,
 la 5,7-dichloro-4-(2,4-difluorophénoxy)quinoléine,
 50 la 5,7-dichloro-4-(2-nitrophénoxy)quinoléine,
 la 5,7-dichloro-4-[2-(trifluorométhyl)phénoxy]quinoléine,
 la 5,7-dichloro-4-(2-fluorophénoxy)quinoléine,
 la 5,7-dichloro-4-(2-chlorophénoxy)quinoléine,
 la 5,7-dichloro-4-(2-cyanophénoxy)quinoléine,
 55 la 5,7-dichloro-4-(2-chloro-4-fluorophénoxy)quinoléine,
 la 5,7-dichloro-4-(3-bromophénoxy)quinoléine,
 la 5,7-dichloro-4-phénoxyquinoléine, ou
 le 4-[(5,7-dichloro-4-quinolyl)oxy]benzonitrile.

15. Composé conforme à la revendication 6, qui est :

- 5 la 8-chloro-4-(2-chlorophénoxy)quinoléine,
la 8-chloro-4-[2-(trifluorométhyl)phénoxy]quinoléine,
la 4-(2-bromophénoxy)-8-chloroquinoléine,
la 8-chloro-4-(2-fluorophénoxy)quinoléine,
la 8-chloro-4-(2-chloro-4-fluorophénoxy)quinoléine,
la 8-chloro-4-(4-isopropylphénoxy)quinoléine,
10 la 8-chloro-4-(2,4-dichlorophénoxy)quinoléine,
la 8-chloro-4-(2-cyanophénoxy)quinoléine,
la 8-chloro-4-(2-iodophénoxy)quinoléine,
la 8-chloro-4-(2,4-difluorophénoxy)quinoléine,
la 8-chloro-4-(3-chlorophénoxy)quinoléine,
la 8-chloro-4-(2-méthylphénoxy)quinoléine.
15 la 8-chloro-4-(2,6-dichlorophénoxy)quinoléine,
la 8-chloro-4-(2-méthoxyphénoxy)quinoléine,
la 8-chloro-4-(4-méthoxyphénoxy)quinoléine,
la 8-chloro-4-(2,4-dichloro-6-fluorophénoxy)quinoléine,
la 8-chloro-4-(2-éthoxyphénoxy)quinoléine,
20 la 8-chloro-4-(4-fluoro-2-méthylphénoxy)quinoléine,
la 8-chloro-4-(4-chloro-2-fluorophénoxy)quinoléine,
la 8-chloro-4-(2,4-dibromophénoxy)quinoléine,
la 8-chloro-4-(4-fluoro-2-nitrophénoxy)quinoléine,
la 8-chloro-4-(2,4,6-trichlorophénoxy)quinoléine,
25 la 8-chloro-4-(2-nitrophénoxy)quinoléine,
la 8-chloro-4-(2,6-dibromo-4-fluorophénoxy)quinoléine,
la 8-chloro-4-(3-méthylphénoxy)quinoléine,
la 8-chloro-4-(4-éthoxyphénoxy)quinoléine,
la 8-chloro-4-(4-chloro-2-méthylphénoxy)quinoléine,
30 la 8-chloro-4-(4-chloro-3,5-diméthylphénoxy)quinoléine,
la 8-chloro-4-(4-chloro-2-nitrophénoxy)quinoléine,
la 8-chloro-4-(2-éthylphénoxy)quinoléine,
la 8-chloro-4-[2-(méthylthio)phénoxy]quinoléine,
la 8-chloro-4-(4-méthylphénoxy)quinoléine,
35 la 8-chloro-4-(2,3-diméthylphénoxy)quinoléine,
la 8-chloro-4-(3,4-diméthylphénoxy)quinoléine,
la 8-chloro-4-[4-(trifluorométhoxy)phénoxy]quinoléine,
la 8-chloro-4-(2,5-dichlorophénoxy)quinoléine.
la 8-chloro-4-(2,6-diméthylphénoxy)quinoléine,
40 la 8-chloro-4-(3,5-diméthylphénoxy)quinoléine,
la 8-chloro-4-(2-chloro-6-méthylphénoxy)quinoléine,
la 8-chloro-4-(2,5-diméthylphénoxy)quinoléine.
la 8-chloro-4-[2-chloro-5-(trifluorométhyl)phénoxy]quinoléine,
la 8-chloro-4-(2-chloro-4-nitrophénoxy)quinoline, ou
45 la 8-chloro-4-(4-éthylphénoxy)quinoléine.

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